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Alembic Club Reprints—No. 12

THE
LIQUEFACTION OF GASES

PAPERS
BY
MICHAEL FARADAY, F.R.S.
(1823-1845)

WITH AN APPENDIX
CONSISTING OF
PAPERS BY THOMAS NORTHMORE
ON THE COMPRESSION OF GASES
(1805-1806)

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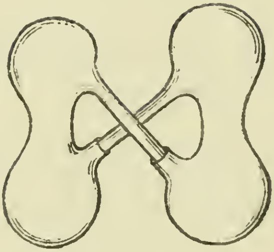

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PREFACE

The papers by Faraday on the Liquefaction of Gases, here reprinted, give an account of the earliest work carried out at the Royal Institution on that most interesting and important subject, with which the Institution was more or less intimately associated, at intervals, for upwards of a century. The extreme beauty and simplicity of Faraday's experiments, as well as the peculiarly felicitous manner in which his various experiments are described, render these papers especially instructive, and suitable for reproduction in the series to which this little volume belongs.

It was considered advisable to reprint Faraday's Historical Statement respecting the Liquefaction of Gases, and, for the sake of greater completeness, to include, in the form of an Appendix, the papers of Mr Northmore which are particularly referred to in that Statement.

L. D.

I. ON FLUID CHLORINE.*

Read March 13, 1823.

IT is well known that before the year 1810, the solid substance obtained by exposing chlorine, as usually procured, to a low temperature, was considered as the gas itself reduced into that form; and that Sir HUMPHRY DAVY first showed it to be a hydrate, the pure dry gas not being condensible even at a temperature of – 40° F.†

I took advantage of the late cold weather to procure crystals of this substance for the purpose of analysis. The results are contained in a short paper in the Quarterly Journal of Science, Vol. XV. Its composition is very nearly 27.7 chlorine, 72.3 water, or 1 proportional of chlorine, and 10 of water.

The President of the Royal Society having honoured me by looking at these conclusions, suggested, that an exposure of the substance to heat under pressure, would probably lead to interesting results; the following experiments were commenced at his request. Some hydrate of chlorine was prepared, and being dried as well as could be by pressure in bibulous paper, was introduced into a sealed glass tube, the upper end of which was then hermetically closed. Being placed in water at 60°, it underwent no change; but when put into water at 100°, the substance fused, the tube became filled with a bright yellow atmosphere, and, on examination, was found to contain two fluid substances: the one, about three-fourths of the whole, was of a faint yellow colour, having very much the appearance of water; the remaining fourth was a heavy bright yellow fluid, lying at the bottom of the former, without any apparent tendency to mix with it. As the tube cooled, the yellow atmosphere condensed into more of the yellow fluid, which floated in a film on the pale fluid, looking very like chloride of nitrogen; and at 70° the pale portion congealed, although even at 32° the yellow portion did not solidify. Heated up to 100° the yellow fluid appeared to boil, and again produced the bright coloured atmosphere.

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* [From Philosophical Transactions for 1823, Vol. 113, pp. 160-165.]

† [See Alembic Club Reprints, No. 9, p. 58.]

By putting the hydrate into a bent tube, afterwards hermetically sealed, I found it easy, after decomposing it by a heat of 100°, to distil the yellow fluid to one end of the tube, and so separate it from the remaining portion. In this way a more complete decomposition of the hydrate was effected, and, when the whole was allowed to cool, neither of the fluids solidified at temperatures above 34°, and the yellow portion not even at 0°. When the two were mixed together they gradually combined at temperatures below 60°, and formed the same solid substance as that first introduced. If, when the fluids were separated, the tube was cut in the middle, the parts flew asunder as if with an explosion, the whole of the yellow portion disappeared, and there was a powerful atmosphere of chlorine produced; the pale portion on the contrary remained, and when examined, proved to be a weak solution of chlorine in water, with a little muriatic acid, probably from the impurity of the hydrate used. When that end of the tube in which the yellow fluid lay was broken under a jar of water, there was an immediate production of chlorine gas.

I at first thought that muriatic acid and euchlorine had been formed; then, that two new hydrates of chlorine had been produced; but at last I suspected that the chlorine had been entirely separated from the water by the heat, and condensed into a dry fluid by the mere pressure of its own abundant vapour. If that were true, it followed, that chlorine gas, when compressed, should be condensed into the same fluid, and, as the atmosphere in the tube in which the fluid lay was not very yellow at 50° or 60°, it seemed probable that the pressure required was not beyond what could readily be obtained by a condensing syringe. A long tube was therefore furnished with a cap and stop-cock, then exhausted of air and filled with chlorine, and being held vertically with the syringe upwards, air was forced in, which thrust the chlorine to the bottom of the tube, and gave a pressure of about 4 atmospheres. Being now cooled, there was an immediate deposit in films, which appeared to be hydrate, formed by water contained in the gas and vessels, but some of the yellow fluid was also produced. As this however might also contain a portion of the water present, a perfectly dry tube and apparatus were taken, and the chlorine left for some time over a bath of sulphuric acid before it was introduced. Upon throwing in air and giving pressure, there was now no solid film formed, but the clear yellow fluid was deposited, and more abundantly still upon cooling. After remaining some time it disappeared, having gradually mixed with the atmosphere above it, but every repetition of the experiment produced the same results.

Presuming that I had now a right to consider the yellow fluid as pure chlorine in the liquid state, I proceeded to examine its properties, as well as I could when obtained by heat from the hydrate. However obtained, it always appears very limpid and fluid, and excessively volatile at common pressure. A portion was cooled in its tube to 0°: it remained fluid. The tube was then opened, when a part immediately flew off, leaving the rest so cooled by the evaporation as to remain a fluid under the atmospheric pressure. The temperature could not have been higher than – 40° in this case; as Sir Humphry Davy has shown that dry chlorine does not condense at that temperature under common pressure. Another tube was opened at a temperature of 50°; a part of the chlorine volatilised, and cooled the tube so much as to condense the atmospheric vapour on it as ice.

A tube having the water at one end and the chlorine at the other was weighed, and then cut in two; the chlorine immediately flew off, and the loss being ascertained was found to be 1.6 grains: the water left was examined and found to contain some chlorine: its weight was ascertained to be 5.4 grains. These proportions, however, must not be considered as indicative of the true composition of hydrate of chlorine; for, from the mildness of the weather during the time when these experiments were made, it was impossible to collect the crystals of hydrate, press, and transfer them, without losing much chlorine; and it is also impossible to separate the chlorine and water in the tube perfectly, or keep them separate, as the atmosphere within will combine with the water, and gradually reform the hydrate.

Before cutting the tube, another tube had been prepared exactly like it in form and size, and a portion of water introduced into it, as near as the eye could judge, of the same bulk as the fluid chlorine: this water was found to weigh 1.2 grains; a result, which, if it may be trusted, would give the specific gravity of fluid chlorine as 1.33; and from its appearance in, and on water, this cannot be far wrong.

Note on the Condensation of Muriatic Acid Gas into the liquid form. By Sir H. DAVY, *Bart., Pres. R.S.*

IN desiring Mr. Faraday to expose the hydrate of chlorine to heat in a closed glass tube, it occurred to me, that one of three things would happen; that it would become fluid as a hydrate; or that a decomposition of water would occur, and euchlorine or muriatic acid be formed; or that the chlorine would separate in a condensed state. This last result having been obtained, it evidently led to other researches of the same kind. I shall hope, on a future occasion, to detail some general views on the subject of these researches. I shall now merely mention, that by sealing the muriate of ammonia and sulphuric acid in a strong glass tube, and causing them to act upon each other, I have procured liquid muriatic acid: and by substituting carbonate for muriate of ammonia, I have no doubt that carbonic acid may be obtained, though in the only trial I have made the tube burst. I have requested Mr. Faraday to pursue these experiments, and to extend them to all the gases which are of considerable density, or to any extent soluble in water; and I hope soon to be able to lay an account of his results, with some applications of them that I propose to make, before the Society.

I cannot conclude this note without observing, that the generation of elastic substances in close vessels, either with or without heat, offers much more powerful means of approximating their molecules than those dependent upon the application of cold, whether natural or artificial: for, as gases diminish only about $\frac{1}{480}$ in volume for every — degree of Fahrenheit's scale, beginning at ordinary temperatures, a very slight condensation only can be produced by the most powerful freezing mixtures, not half as much as would result from the application of a strong flame to one part of a glass tube, the other part being of ordinary temperature: and when attempts are made to condense gases into fluids by sudden mechanical compression, the heat, instantly generated, presents a formidable obstacle to the success of the experiment; whereas, in the compression resulting from their slow generation in close vessels, if the process be conducted with common precautions, there is no source of difficulty or danger; and it may be easily assisted by artificial cold in cases when gases approach near to that point of compression and temperature at which they become vapours

II. ON THE CONDENSATION OF SEVERAL GASES INTO LIQUIDS.*

Read April 10, 1823.

I HAD the honour, a few weeks since, of submitting to the Royal Society a paper on the reduction of chlorine to the liquid state. An important note was added to the paper by the President, on the general application of the means used in this case to the reduction of other gaseous bodies to the liquid state; and in illustration of the process, the production of liquid muriatic acid was described. Sir HUMPHRY DAVY did me the honour to request I would continue the experiments, which I have done under his general direction, and the following are some of the results already obtained:

Sulphurous Acid.

Mercury and concentrated sulphuric acid were sealed up in a bent tube, and, being brought to one end, heat was carefully applied, whilst the other end was preserved cool by wet bibulous paper. Sulphurous acid gas was produced where the heat acted, and was condensed by the sulphuric acid above; but, when the latter had become saturated, the sulphurous acid passed to the cold end of the tube, and was condensed into a liquid. When the whole tube was cold, if the sulphurous acid were returned on to the mixture of sulphuric acid and sulphate of mercury, a portion was re-absorbed, but the rest remained on it without mixing.

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* [From Philosophical Transactions for 1823, Vol. 113, pp. 189-198.]

Liquid sulphurous acid is very limpid and colourless, and highly fluid. Its refractive power, obtained by comparing it in water and other media, with water contained in a similar tube, appeared to be nearly equal to that ot water. It does not solidify or become adhesive at a temperature of 0° F. When a tube containing it was opened, the contents did not rush out as with explosion, but a portion of the liquid evaporated rapidly, cooling another portion so much as to leave it in the fluid state at common barometric pressure. It was however rapidly dissipated, not producing visible fumes, but producing the odour of pure sulphurous acid, and leaving the tube quite dry. A portion of the vapour of the fluid received over a mercurial bath, and examined, proved to be sulphurous acid gas. A piece of ice dropped into the fluid instantly made it boil, from the heat communicated by it.

To prove in an unexceptionable manner that the fluid was pure sulphurous acid, some sulphurous acid gas was carefully prepared over mercury, and a long tube perfectly dry, and closed at one end, being exhausted, was filled with it; more sulphurous acid was then thrown in by a condensing syringe, till there were three or four atmospheres; the tube remained perfectly clear and dry, but on cooling one end to 0°, the fluid sulphurous acid condensed, and in all its characters was like that prepared by the former process.

A small gage was attached to a tube in which sulphurous acid was afterwards formed, and at a temperature of 45° F. the pressure within the tube was equal to three atmospheres, there being a portion of liquid sulphurous acid present: but as the common air had not been excluded when the tube was sealed, nearly one atmosphere must be due to its presence, so that sulphurous acid vapour exerts a pressure of about two atmospheres at 45° F. Its specific gravity was nearly 1.42.*

Sulphuretted hydrogen.

A tube being bent, and sealed at the shorter end, strong muriatic acid was poured in through a small funnel, so as nearly to fill the short leg without soiling the long one. A piece of platinum foil was then crumpled up and pushed in, and upon that were put fragments of sulphuret of iron, until the tube was nearly full. In this way action was prevented until the tube was sealed. If it once commences, it is almost impossible to close the tube in a manner sufficiently strong, because of the pressing out of the gas. When closed, the muriatic acid was made to run on to the sulphuret of iron, and then left for a day or two. At the end of that time, much proto-muriate of iron had formed, and on placing the clean end of the tube in a mixture of ice and salt, warming the other end if necessary by a little water, sulphuretted hydrogen in the liquid state distilled over.

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* I am indebted to Mr. DAVIES GILBERT, who examined with much attention the results of these experiments, for the suggestion of the means adopted to obtain the specific gravity of some of these fluids. A number of small glass bulbs were blown and hermetically sealed; they were then thrown into alcohol, water, sulphuric acid, or mixtures of these, and when any one was found of the same specific gravity as the fluid in which it was immersed, the specific gravity of the fluid was taken: thus a number of hydrometrical bulbs were obtained; these were introduced into the tubes in which the substances were to be liberated; and ultimately, the dry liquids obtained, in contact with them. It was then observed whether they floated or not, and a second set of experiments were made with bulbs lighter or heavier as required, until a near approximation was obtained. Many of the tubes burst in the experiments, and in others difficulties occurred from the accidental fouling of the bulb by the contents of the tube. One source of error may be mentioned in addition to those which are obvious, namely, the alteration of the bulk of the bulb by its submission to the pressure required to keep the substance in the fluid state.

The liquid sulphuretted hydrogen was colourless, limpid, and excessively fluid. Ether, when compared with it in similar tubes, appeared tenacious and oily. It did not mix with the rest of the fluid in the tube, which was no doubt saturated, but remained standing on it. When a tube containing it was opened, the liquid immediately rushed into vapour; and this being done under water, and the vapour collected and examined, it proved to be sulphuretted hydrogen gas. As the temperature of a tube containing some of it rose from 0° to 45°, part of the fluid rose in vapour, and its bulk diminished; but there was no other change: it did not seem more adhesive at 0° than at 45°. Its refractive power appeared to be rather greater than that of water; it decidedly surpassed that of sulphurous acid. A small gage being introduced into a tube in which liquid sulphuretted hydrogen was afterwards produced, it was found that the pressure of its vapour was nearly equal to 17 atmospheres at the temperature of 50°.

The gages used were made by drawing out some tubes at the blow-pipe table until they were capillary, and of a trumpet form; they were graduated by bringing a small portion of mercury successively into their different parts; they were then sealed at the fine end, and a portion of mercury placed in the broad end ; and in this state they were placed in the tubes, so that none of the substances used, or produced, could get to the mercury, or pass by it to the inside of the gage. In estimating the number of atmospheres, one has always been subtracted for the air left in the tube.

The specific gravity of sulphuretted hydrogen appeared to be 0.9.

Carbonic acid.

The materials used in the production of carbonic acid, were carbonate of ammonia and concentrated sulphuric acid ; the manipulation was like that described for sulphuretted hydrogen. Much stronger tubes are however required for carbonic acid than for any of the former substances, and there is none which has produced so many or more powerful explosions. Tubes which have held fluid carbonic acid well for two or three weeks together, have, upon some increase in the warmth of the weather, spontaneously exploded with great violence ; and the precautions of glass masks, goggles, &c. which are at all times necessary in pursuing these experiments, are particularly so with carbonic acid.

Carbonic acid is a limpid colourless body, extremely fluid, and floating upon the other contents of the tube. It distils readily and rapidly at the difference of temperature between 32° and 0°. Its refractive power is much less than that of water. No diminution of temperature to which I have been able to submit it, has altered its appearance. In endeavouring to open the tubes at one end, they have uniformly burst into fragments, with powerful explosions. By inclosing a gage in a tube in which fluid carbonic acid was afterwards produced, it was found that its vapour exerted a pressure of 36 atmospheres at a temperature of 32°.

It may be questioned, perhaps, whether this and other similar fluids obtained from materials containing water, do not contain a portion of that fluid; in as much as its absence has not been proved, as it may be with chlorine, sulphurous acid, cyanogen, and ammonia. But besides the analogy which exists between the latter and the former, it may also be observed in favour of their dryness, that any diminution of temperature causes the deposition of a fluid from the atmosphere, precisely like that previously obtained; and there is no reason for supposing that these various atmospheres, remaining as they do in contact with concentrated sulphuric acid, are not as dry as atmospheres of the same kind would be over sulphuric acid at common pressure.

Euchlorine.

Fluid euchlorine was obtained by inclosing chlorate of potash and sulphuric acid in a tube, and leaving them to act on each other for 24 hours. In that time there had been much action, the mixture was of a dark reddish brown, and the atmosphere of a bright yellow colour. The mixture was then heated up to 100°, and the unoccupied end of the tube cooled to 0°; by degrees the mixture lost its dark colour, and a very fluid ethereal looking substance condensed. It was not miscible with a small portion of the sulphuric acid which lay beneath it; but when returned on to the mass of salt and acid, it was gradually absorbed, rendering the mixture of a much deeper colour even than itself.

Euchlorine thus obtained is a very fluid transparent substance, of a deep yellow colour. A tube containing a portion of it in the clean end, was opened at the opposite extremity; there was a rush of euchlorine vapour, but the salt plugged up the aperture: whilst clearing this away, the whole tube burst with a violent explosion, except the small end in a cloth in my hand, where the euchlorine previously lay, but the fluid had all disappeared.

Nitrous oxide.

Some nitrate of ammonia, previously made as dry as could be by partial decomposition, by heat in the air, was sealed up in a bent tube, and then heated in one end, the other being preserved cool. By repeating the distillation once or twice in this way, it was found, on after-examination, that very little of the salt remained undecomposed. The process requires care. I have had many explosions occur with very strong tubes, and at considerable risk.

When the tube is cooled, it is found to contain two fluids, and a very compressed atmosphere. The heavier fluid on examination proved to be water, with a little acid and nitrous oxide in solution; the other was nitrous oxide. It appears in a very liquid, limpid, colourless state; and so volatile that the warmth of the hand generally makes it disappear in vapour. The application of ice and salt condenses abundance of it into the liquid state again. It boils readily by the difference of temperature between 50° and 0°. It does not appear to have any tendency to solidify at – 10°. Its refractive power is very much less than that of water, and less than any fluid that has yet been obtained in these experiments, or than any known fluid. A tube being opened in the air, the nitrous oxide immediately burst into vapour. Another tube opened under water, and the vapour collected and examined, it proved to be nitrous oxide gas. A gage being introduced into a tube, in which liquid nitrous oxide was afterwards produced, gave the pressure of its vapour as equal to above 50 atmospheres at 45°.

Cyanogen.

Some pure cyanuret of mercury was heated until perfectly dry. A portion was then inclosed in a green glass tube, in the same manner as in former instances, and being collected to one end, was decomposed by heat, whilst the other end was cooled. The cyanogen soon appeared as a liquid: it was limpid, colourless, and very fluid; not altering its state at the temperature of 0°. Its refractive power is rather less, perhaps, than that of water. A tube containing it being opened in the air, the expansion within did not appear to be very great; and the liquid passed with comparative slowness into the state of vapour, producing great cold. The vapour, being collected over mercury, proved to be pure cyanogen.

A tube was sealed up with cyanuret of mercury at one end, and a drop of water at the other; the fluid cyanogen was then produced in contact with the water. It did not mix, at least in any considerable quantity, with that fluid, but floated on it, being lighter, though apparently not so much so as ether would be. In the course of some days, action had taken place, the water had become black, and changes, probably such as are known to take place in an aqueous solution of cyanogen, occurred. The pressure of the vapour of cyanogen appeared by the gage to be 3.6 or 3.7 atmospheres at 45° F. Its specific gravity was nearly 0.9.

Ammonia.

In searching after liquid ammonia, it became necessary, though difficult, to find some dry source of that substance; and I at last resorted to a compound of it, which I had occasion to notice some years since with chloride of silver.* When dry chloride of silver is put into ammoniacal gas, as dry as it can be made, it absorbs a large quantity of it; 100 grains condensing above 130 cubical inches of the gas: but the compound thus formed is decomposed by a temperature of 100° F. or upwards. A portion of this compound was sealed up in a bent tube and heated in one leg, whilst the other was cooled by ice or water. The compound thus heated under pressure fused at a comparatively low temperature, and boiled up, giving off ammoniacal gas, which condensed at the opposite end into a liquid.

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* Quarterly Journal of Science, Vol. V. p. 74.

Liquid ammonia thus obtained was colourless, transparent, and very fluid. Its refractive power surpassed that of any other of the fluids described, and that also of water itself. From the way in which it was obtained, it was evidently as free from water as ammonia in any state could be. When the chloride of silver is allowed to cool, the ammonia immediately returns to it, combining with it, and producing the original compound. During this action a curious combination of effects takes place: as the chloride absorbs the ammonia, heat is produced, the temperature rising up nearly to 100°; whilst a few inches off, at the opposite end of the tube, considerable cold is produced by the evaporation of the fluid. When the whole is retained at the temperature of 60°, the ammonia boils till it is dissipated and re-combined. The pressure of the vapour of ammonia is equal to about 6.5 atmospheres at 50°. Its specific gravity was 0.76.

Muriatic acid.

When made from pure muriate of ammonia and sulphuric acid, liquid muriatic acid is obtained colourless, as Sir HUMPHRY DAVY had anticipated. Its refractive power is greater than that of nitrous oxide, but less than that of water; it is nearly equal to that of carbonic acid.

The pressure of its vapour at the temperature of 50°, is equal to about 40 atmospheres.

Chlorine.

The refractive power of fluid chlorine is rather less than that of water. The pressure of its vapour at 60° is nearly equal to 4 atmospheres.

Attempts have been made to obtain hydrogen, oxygen, fluoboracic, fluosilicic, and phosphuretted hydrogen gases in the liquid state; but though all of them have been subjected to great pressure, they have as yet resisted condensation. The difficulty with regard to fluoboric gas consists, probably, in its affinity for sulphuric acid, which, as Dr. DAVY has shown, is so great as to raise the sulphuric acid with it in vapour. The experiments will however be continued on these and other gases, in the hopes that some of them, at least, will ultimately condense.

III. HISTORICAL STATEMENT RESPECTING THE LIQUEFACTION OF GASES*.

I WAS not aware at the time when I first observed the liquefaction of chlorine gas†, nor until very lately, that any of the class of bodies called *gases*, had been reduced into the fluid form; but, having during the last few weeks sought for instances where such results might have been afforded without the knowledge of the experimenter, I was surprised to find several recorded cases. I have thought it right therefore to bring these cases together, and only justice to endeavour to secure for them a more general attention, than they appear as yet to have gained. I shall notice in chronological order, the fruitless, as well as the successful, attempts, and those which probably occurred without being observed, as well as those which were remarked and described as such.

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* [From *The Quarterly Journal of Science*, vol. xvi. (January 1824), pp. 229-240.]

† *Phil. Transactions*, 1823, pp. 160, 189.

Carbonic Acid, &c.—The *Philosophical Transactions* for 1797, contain, p. 222, an account of experiments made by Count Rumford, to determine the force of fired gunpowder. Dissatisfied both with the deductions drawn, and the means used previously, that philosopher proceeded to fire gunpowder in cylinders of a known diameter and capacity, and closed by a valve loaded with a weight that could be varied at pleasure. By making the vessel strong enough and the weight sufficiently heavy, he succeeded in confining the products within the space previously occupied by the powder. The Count's object induced him to vary the quantity of gunpowder in different experiments, and to estimate the force exerted only at the moment of ignition, when it was at its maximum. This force which he found to be prodigious, he attributes to aqueous vapour intensely heated, and makes no reference to the force of the gaseous bodies evolved. Without considering the phenomena which it is the Count's object to investigate, it may be remarked, that in many of the experiments made by him, some of the gases, and especially carbonic acid gas, were probably reduced to the liquid state. The Count says,

"When the force of the generated elastic vapour was sufficient to raise the weight, the explosion was attended by a very sharp and surprisingly loud report; but when the weight was not raised, as also when it was only a little moved, but not sufficiently to permit the leather stopper to be driven quite out of the bore, and the elastic fluid to make its escape, the report was scarcely audible at the distance of a few paces, and did not at all resemble the report which commonly attends the explosion of gunpowder. It was more like the noise which attends the breaking of a small glass tube, than any thing else to which it could be compared. In many of the experiments, in which the elastic vapour was confined, this feeble report attending the explosion of the powder, was immediately followed by another noise totally different from it, which appeared to be occasioned by the falling back of the weight upon the end of the barrel, after it had been a little raised, but not sufficiently to permit the leather stopper to be driven quite out of the bore. In some of these experiments a very small part only of the generated elastic fluid made its escape, in these cases the report was of a peculiar kind, and though perfectly audible at some considerable distance, yet not at all resembling the report of a musket. It was rather a very strong sudden hissing, than a clear distinct and sharp report."

In another place it is said, "What was very remarkable in all these experiments, in which the generated elastic vapour was completely confined, was the small degree of expansive force which this vapour appeared to possess, after it had been suffered to remain a few minutes, or even only a few seconds, confined in the barrel; for upon raising the weight, by means of its lever, and suffering this vapour to escape, instead of escaping with a loud report it rushed out with a hissing noise, hardly so loud or so sharp as the report of a common air-gun, and its effects against the leather stopper, by which it assisted in raising the weight, were so very feeble as not to be sensible." This the Count attributes to the formation of a hard mass, like a stone, within the cylinder, occasioned by the condensation of what was, at the moment of ignition, an elastic fluid. Such a substance was always found in these cases; but when the explosion raised the weight and blew out the stopper, nothing of this kind remained.

The effects here described both of elastic force and its cessation on cooling, may evidently be referred as much to carbonic acid and perhaps other gases as to water. The strong sudden hissing observed as occurring when only a little of the products escaped, may have been due to the passage of the gases into the air, with comparatively but little water, the circumstances being such as were not sufficient to confine the former, though they might the latter; for it cannot be doubted but that in similar circumstances, the elastic force of carbonic acid would far surpass that of water. Count Rumford says, that the gunpowder made use of, when well shaken together, occupied rather less space than an equal weight of water. The quantity of residuum before referred to, left by a given weight of gunpowder, is not mentioned, so that the actual space occupied by the vapour of water, carbonic acid, &c., at the moment of ignition, cannot be inferred; there can, however, be but little doubt that when perfectly confined they were in the state of the substances, in M. Cagniard de la Tour's experiments*.

When allowed to remain a few minutes, or even seconds, the expansive force at first observed, diminished exceedingly, so as scarcely to surpass that of the air in a charged air-gun. Of course all that was due to the vaporization of water and some of the other products would cease, as soon as the mass of metal had absorbed the heat, and they would concrete into the hard substance found in the cylinder: but it does not seem too much to suppose, that so much carbonic acid was generated in the combustion, as would, if confined, on the cooling of the apparatus, have been equal to many atmospheres, but that being condensible, a part became liquid, and thus assisted in reducing the force within, to what it was found to be.

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* See vol. xv. p. 145, of this Journal.

Ammonia.—I find the condensation of ammoniacal gas referred to in *Thomson's System*, first edition, i. 405, and other editions; *Henry's Chemistry*, i. 237; *Accum's Chemistry*, i. 310; *Murray's Chemistry*, ii. 73; and *Thenard's Traité de Chimie*, ii. 133. Mr. Accum refers to the experiments of Fourcroy and Vauquelin, *Ann. de Chimie*, xxix. 289, but has mistaken their object. Those chemists used highly saturated solution of ammonia, see pp. 281, 286, and not the gas; and their experiments on gases, namely, sulphurous acid gas, muriatic acid gas, and sulphuretted hydrogen gas, they state were fruitless, p. 287. "All we can say is, that the condensation of most of these gases was above three fourths of their volume."

Thomson, Henry, Murray, and, I suppose, Thenard, refer to the experiments of Guyton de Morveau, *Ann. de Chimie*, xxix. 291, 297. Thomson states the result of liquefaction at a temperature of – 45°, without referring to the doubt, that Morveau himself raises, respecting the presence of water in the gas; but Murray, Henry, and Thenard, in their statements notice its probable presence. Morveau's experiment was made in the following manner: a glass retort was charged with the usual mixture of muriate of ammonia, and quick lime, the former material being sublimed, and the latter carefully made from white marble, so as to exclude water as much as possible. The beak of the retort was then adapted to an apparatus consisting of two balloons, and two flasks successively connected together, and luted by fat lute. The balloons were empty, the first flask contained mercury, the second, water. Heat was then applied to the retort, and the first globe cooled to – 21.25°C., aqueous vapours soon rose, which condensed as water in the neck of the retort, and as ice in the first balloon. Continuing the heat, ammoniacal gas was disengaged, and it escaped by the last flask containing water, without anything being perceived in the second balloon. This balloon was then cooled to – 43.25° C., and then drops of a fluid lined its interior, and ultimately united at the bottom of the vessel. When the thermometer in the cooling mixture stood at – 36.25°C., the fluid already deposited preserved its state, but no further portions were added to it; reducing the temperature again to – 41°C., and hastening the disengagement of ammoniacal gas, the liquid in the second balloon augmented in volume. Very little gas escaped from the last flask, and the pressure inwards was such as to force the oil of the lute into the balloon where it congealed. Finally, the apparatus was left to regain the temperature of the atmosphere, and as it approached to it, the liquid of the second balloon became gaseous. The fluid in the first balloon became liquid, as soon as the temperature had reached – 21.25°C.

M. Morveau remarks on this experiment, that it appears certain that ammoniacal gas made as dry as it can be, by passing into a vessel in which water would be frozen, and reduced to a temperature of – 21°C., condenses into a liquid at the temperature of – 48°C., and resumes its elastic form again as the temperature is raised; but he proposes to repeat the experiment and examine whether a portion of the gas so dried, when received over mercury would not yield water to well calcined potash, "for as it is seen that water charged with a little of the gas, remained liquid in the first balloon, at a temperature of – 21°, it is possible that a much smaller quantity of water united to a much larger quantity of the gas, would become capable of resisting a temperature of – 48°C.

Sir H. Davy, who refers to this experiment in his *Elements of Chemical Philosophy*, p. 267, urges the uncertainty attending it, on the same grounds that Morveau himself had done; and now that the strength of the vapour of dry liquid ammonia is known, it cannot be doubted that M. Morveau had obtained in his second balloon only a very concentrated solution of ammonia in water. I find that the strength of the vapour of ammonia dried by potash, is equal to about that of 6.5 atmospheres at 50° F*. and according to all analogy it would require a very intense degree of cold, and one at present beyond our means, to compensate this power and act as an equivalent to it.

Sulphurous Acid Gas.—It is said that sulphurous acid gas has been condensed into a fluid by Monge and Clouet, but I have not been able to find the description of their process. It is referred to by Thomson, in his *System*, first edition, ii. 24, and in subsequent editions; by Henry, in his *Elements*, i. 341; by Accum, in his *Chemistry*, i. 319; by Aikin, *Chemical Dictionary*, ii. 391; by Nicholson, *Chemical Dictionary*, article, gas (Sulphurous acid); and by Murray, in his *System*, ii. 405. All these authors mention the simultaneous application of cold and pressure, but Thomson alone refers to any authority, and that is Fourcroy, ii. 74.

It is curious that Fourcroy does not, however, mention condensation as one of the means employed by Monge and Clouet, but merely says the gas is capable of liquefaction at 28° of cold. "This latter property," he adds, "discovered by citizens Monge and Clouet, and by which it is distinguished from all the other gases, appears to be owing to the water which it holds in solution, and to which it adheres so strongly as to prevent an accurate estimate of the proportions of its radical and acidifying principles."

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* *Philosophical Transactions*, 1823, p. 197.

Notwithstanding Fourcroy's objection, there can be but little reason to doubt that Monge and Clouet did actually condense the gas, for I have since found that from the small elastic force of its vapour at common temperatures (being equal to that of about two atmospheres only *) a comparatively moderate diminution of temperature is sufficient to retain it fluid at common pressure, or a moderate additional pressure to retain it so at common temperature; so that whether these philosophers applied cold only as Fourcroy mentions, or cold and pressure, as stated by the other chemists, they would succeed in obtaining it in the liquid form.

Chlorine.—M. de Morveau, whilst engaged on the application of the means best adapted to destroy putrid effluvia and contagious miasmata, was led to the introduction of chlorine as the one most excellent for this purpose; and he proposed the use of phials, containing the requisite materials, as sources of the substance. One described in his *Traité des Moyens de désinfecter l'air* (1801), was of the capacity of two cubical inches nearly; about 62 grains of black oxide of manganese in coarse powder was introduced, and then the bottle two-thirds filled with nitro-muriatic acid; it was shaken, and in a short time chlorine was abundantly disengaged. M. Morveau remarks upon the facility with which the chlorine is retained in these bottles; one, thus prepared, and forgotten, when opened at the end of eight years, gave an abundant odour of chlorine.

I had an impression on my mind that M. de Morveau had proposed the use of phials similarly charged, but made strong, well stoppered, and confined by a screw in a frame, so that no gas should escape, except when the screw and stopper were loosened; but I have searched for an account of such phials without being able to find any. If such have been made, it is very probable that in some circumstances, liquid chlorine has existed in them, for as its vapour at 60°F. has only a force of about four atmospheres*, a charge of materials might be expected frequently to yield much more chlorine than enough to fill the space, and saturate the fluid present; and the excess would of course take the liquid form. If such vessels have not been made, our present knowledge of the strength of the vapour of chlorine will enable us to construct them of a much more convenient and portable form than has yet been given to them.

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* *Philosophical Transactions*, 1823, p. 192.

Arseniuretted Hydrogen.—This is a gas which it is said has been condensed so long since as 1805. The experiment was made by Stromeyer, and was communicated, with many other results relating to the same gas, to the Göttingen Society, Oct. 12, 1805. See *Nicholson's Journal*, xix. 382; also, *Thenard Traité de Chimie*, i. 373; *Brande's Manual*, ii. 212; and *Annales de Chimie*, lxiv. 303. None of these contain the original experiment; but the following quotation is from *Nicholson's Journal*. The gas was obtained over the pneumatic apparatus, by digesting an alloy of fifteen parts tin and one part arsenic, in strong muriatic acid. "Though the arsenicated hydrogen gas retains its aëriform state under every known degree of atmospheric temperature and pressure, Professor Stromeyer condensed it so far as to reduce it in part to a liquid, by immersing it in a mixture of snow and muriate of lime, in which several pounds of quicksilver had been frozen in the course of a few minutes." From the circumstance of its being reduced only in part to a liquid, we may be led to suspect that it was rather the moisture of the gas that was condensed than the gas itself; a conjecture which is strengthened in my mind from finding that a pressure of three atmospheres was insufficient to liquefy the gas at a temperature of 0°F.

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* *Ibid.* p. 198.

Chlorine.—The most remarkable and direct experiments I have yet met with in the course of my search after such as were connected with the condensation of gases into liquids, are a series made by Mr. Northmore, in the years 1805-6. It was expected by this gentleman "that the various affinities which take place among the gases under the common pressure of the atmosphere, would undergo considerable alteration by the influence of condensation;" and it was with this in view that the experiments were made and described. The results of liquefaction were therefore incidental, but at present it is only of them I wish to take notice. Mr. Northmore's papers may be found in *Nicholson's Journal*, xii. 368, xiii. 233. In the first is described his apparatus, namely, a brass condensing pump; pear-shaped glass receivers, containing from three and a half to five cubic inches, and a quarter of an inch thick; and occasionally a syphon gauge. Sometimes as many as eighteen atmospheres were supposed to have been compressed into the vessel, but it is added, that the quantity cannot be depended on, as the tendency to escape even by the side of the piston, rendered its confinement very difficult.

Now that we know the pressure of the vapour of chlorine, there can be no doubt that the following passage describes a true liquefaction of that gas. "Upon the compression of nearly two pints of oxygenated muriatic acid gas in a receiver, two and a quarter cubic inches capacity, it speedily became converted into a yellow *fluid*, of such extreme volatility, under the common pressure of the atmosphere, that it instantly evaporated upon opening the screw of the receiver; I need not add, that this fluid, so highly concentrated, is of a most insupportable pungency." "There was a trifling residue of a yellowish substance left after the evaporation, which probably arose from a small portion of the oil and grease used in the machine," &c. xiii. 234.

Muriatic Acid.—Operating upon muriatic acid, Mr. Northmore obtained such results as induced him to state he could liquefy it in any quantity, but as the pressure of its vapour at 50°F. is equal to about 40 atmospheres*, he must have been mistaken. The following is his account: "I now proceeded to the muriatic acid gas, and upon the condensation of a small quantity of it, a beautiful green-coloured substance adhered to the side of the receiver, which had all the qualities of muriatic acid; but upon a large quantity, four pints, being condensed, the result was a yellowish green glutinous substance, which does not evaporate, but is instantly absorbed by a few drops of water; it is of a highly pungent quality, being the essence of muriatic acid. As this gas easily becomes fluid, there is little or no elasticity, so that any quantity may be condensed without danger. My method of collecting this and other gases, which are absorbable by water, is by means of an exhausted Florence flask, (and in some cases an empty bladder) connected by a stop cock with the extremity of the retort." xiii. 235. It seems probable that the facility of condensation, and even combination, possessed by muriatic acid gas in contact with oil of turpentine, may belong to it under a little pressure, in contact with common oil, and thus have occasioned the results Mr. Northmore describes.

Sulphurous Acid Gas.—With regard to this gas, Mr.

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* *Philosophical Transactions*, 1823, p. 198.

Northmore says, "having collected about a pint and a half of sulphurous acid gas, I proceeded to condense it in the three cubic inch receiver, but after a very few pumps the forcing piston became immoveable, being completely choked by the operation of the gas. A sufficient quantity had, however, been compressed to form vapour, and a thick slimy fluid, of a dark yellow colour, began to trickle down the sides of the receiver, which immediately evaporated with the most suffocating odour upon the removal of the pressure." xiii. 236. This experiment, Mr. Northmore remarks, corroborates the assertion of Monge and Clouet, that by cold and pressure they had condensed this gas. The fluid above described was evidently contaminated with oil, but from its evaporation on removing the pressure, and from the now ascertained low pressure of the vapour of sulphurous acid, there can be no hesitation in admitting that it was sulphurous acid liquefied.

The results obtained by Mr. Northmore, with chlorine gas and sulphurous acid gas, are referred to by Nicholson, in his *Chemical Dictionary*, 8vo. Articles, Gas (muriatic acid oxygenized) and Gas (sulphurous acid); and that of chlorine is referred to by Murray, in his *System*, ii. 550; although at page 405 of the same volume, he says that, only sulphurous acid "and ammonia of these gases that are at natural temperatures permanently elastic, have been found capable of this reduction."

Carbonic Acid.—Another experiment in which it is very probable that liquid carbonic acid has been produced, is one made by Mr. Babbage, about the year 1813. The object Mr. Babbage had in view, was to ascertain whether pressure would prevent decomposition, and it was expected that either that would be the case, or that decomposition would go on, and the rock be split by the expansive force of carbonic acid gas. The place was Chudley rocks, Devonshire, where the limestone is dark and of a compact texture. A hole, about 30 inches deep and two inches in diameter, was made by the workmen in the usual way, it penetrated directly downwards into the rock; a quantity of strong muriatic acid, equal to perhaps a pint and a half, was then poured in, and immediately a conical wooden plug, that had previously been soaked in tallow, was driven hard into the mouth of the hole. The persons about then retired to a distance to watch the result, but nothing apparent happened, and, after waiting some time, they left the place. The plug was not loosened at the time, nor was any further examination of the state of things made: but it is very probable that if the rock were sufficiently compact in that part, the plug tight, and the muriatic acid in sufficient quantity, that a part of the carbonic acid had condensed into a liquid, and thus, though it permitted the decomposition, prevented that development of power which Mr. Babbage expected would have torn the rock asunder.

Oil Gas Vapour.—An attempt has been made by Mr Gordon, within the last few years, and is still continued, to introduce condensed gas into use in the construction of portable, elegant, and economical gas lamps. Oil gas has been made use of, and, I believe, as many as thirty atmospheres have been thrown into vessels, which, furnished with a stop cock and jet, have afterwards allowed of its gradual expansion and combustion. During the condensation of the gas in this manner, a liquid has been observed to deposit from it. It is not, however, a result of the liquefaction of the gas, but the deposition of a vapour (using the terms gas and vapour in their common acceptation) from it, and when taken out of the vessel it remains a liquid at common temperatures and pressures; may be purified by distillation, in the ordinary way, and will even bear a temperature of 170°F. before it boils, at ordinary pressure. It is the substance referred to by Dr Henry, in the *Philosophical Transactions*, 1821, p. 159.

There is no reason for believing that oil gas, or olefiant gas, has, as yet, been condensed into a liquid, or that it will take that form at common temperatures under a pressure of five, or ten, or even twenty atmospheres. If it were possible, a small, safe, and portable gas lamp would immediately offer itself to us, which might be filled with liquid without being subject to any greater force than the strength of its vapour, and would afford an abundant supply of gas as long as any of the liquid remained. Immediately upon the condensation of cyanogen, which takes place at 50°F. at a pressure under four atmospheres, I made such a lamp with it. It succeeded perfectly, but, of course, either the expense of the gas, the faint light of its flame, or its poisonous qualities, would preclude its application. But we may, perhaps, without being considered extravagant, be allowed to search in the products of oil, resins, coal, &c., distilled, or otherwise treated, with this object in view, for a substance, which being a gas at common temperatures and pressure, shall condense into a liquid, by a pressure of from two to six or eight atmospheres, and which being combustible, shall afford a lamp of the kind described*.

Atmospheric Air.—As my object is to draw attention to the results obtained in the liquefaction of gases before the date of those described in the *Philosophical Transactions* for 1823, I need not, perhaps, refer to the notice given in the *Annals of Philosophy*, *N.S.* vi. 66, of the supposed liquefaction of atmospheric air, by Mr. Perkins, under a pressure of about 1100 atmospheres, but as such a result would be highly interesting, and is the only additional one on the subject I am acquainted with, I am desirous of doing so, as well also to point out the remarkable difference between that result and those which are the subject of this and the other papers referred to. Mr. Perkins informed me that the air upon compression disappeared, and in its place was a small quantity of a fluid, which remained so when the pressure was removed, which had little or no taste, and which did not act on the skin. As far as I could by inquiry make out its nature, it resembled water, but if upon repetition it be found really to be the product of compressed common air, then its fixed nature shews it to be a result of a very different kind to those mentioned above, and necessarily attended by far more important consequences.

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* In reference to the probability of such results, see a paper "On Olefiant Gas." *Annals of Philosophy*, *N.S.* iii. 37.

IV. ON THE LIQUEFACTION AND SOLIDIFICATION OF BODIES GENERALLY EXISTING AS GASES.*

Received December 19, 1844,—*Read January* 9, 1845.

THE experiments formerly made on the liquefaction of gases,† and the results which from time to time have been added to this branch of knowledge, especially by M. THILORIER,‡ have left a constant desire on my mind to renew the investigation. This, with considerations arising out of the apparent simplicity and unity of the molecular constitution of all bodies when in the gaseous or vaporous state, which may be expected, according to the indications given by the experiments of M. Cagniard de la Tour, to pass by some simple law into their liquid state, and also the hope of seeing nitrogen, oxygen, and hydrogen, either as liquid or solid bodies, and the latter probably as a metal, have lately induced me to make many experiments on the subject, and though my success has not been equal to my desire, still I hope some of the results obtained, and the means of obtaining them, may have an interest for the Royal Society; more especially as the application of the latter may be carried much further than I as yet have had opportunity of applying them. My object, like that of some others, was to subject the gases to considerable pressure with considerable depression of temperature. To obtain the pressure, I used mechanical force, applied by two air-pumps fixed to a table. The first pump had a piston of an inch in diameter, and the second a piston of only half an inch in diameter; and these were so associated by a connecting pipe, that the first pump forced the gas into and through the valves of the second, and then the second could be employed to throw forward this gas, already condensed to ten, fifteen, or twenty atmospheres, into its final recipient at a much higher pressure.

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* [From Philosophical Transactions for 1845, Vol. 135, pp. 155–177.]

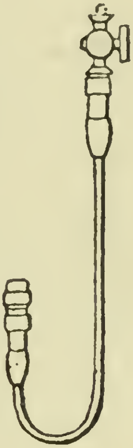
† Philosophical Transactions, 1823, pp. 160, 189.

‡ Annales de Chimie, 1835, lx. 427, 432.

The gases to be experimented with were either prepared and retained in gas holders or gas jars, or else, when the pumps were dispensed with, were evolved in strong glass vessels, and sent under pressure into the condensing tubes. When the gases were over water, or likely to contain water, they passed, in their way from the air-holder to the pump, through a coil of thin glass tube retained in a vessel filled with a good mixture of ice and salt, and therefore at the temperature of 0° Fahr.; the water that was condensed here was all deposited in the first two inches of the coil.

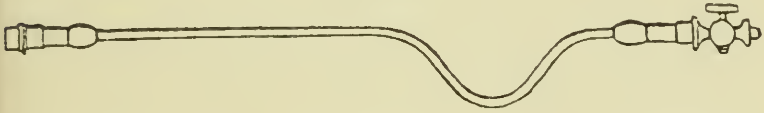
The condensing tubes were of green bottle glass, being from $\frac{1}{6}$th to $\frac{1}{4}$th of an inch external diameter, and from $\frac{1}{12}$d to $\frac{1}{30}$th of an inch in thickness. They were chiefly of two kinds, about eleven and nine inches in length; the one, when horizontal, having a curve downward near one end to dip into a cold bath, and the other, being in form like an inverted siphon, could have the bend cooled also in the same manner when necessary. Into the straight part of the horizontal tube, and the longest leg of the siphon tube, pressure gauges were introduced when required.

Fig. 1.



Caps, stop-cocks and connecting pieces were employed to attach the glass tubes to the pumps, and these, being of brass, were of the usual character of those employed for operations with gas, except that they were small and carefully made. The caps were of such size that the ends of the glass tubes entered freely into them, and had rings or a female screw worm cut in the interior, against which the cement was to adhere. The ends of the glass tubes were roughened by a file, and when a cap was to be fastened on, both it and the end of the tube were made so warm that the cement*, when applied, was thoroughly melted in contact with these parts, before the tube and cap were brought together and finally adjusted

Fig. 2.



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* Five parts of resin, one part of yellow bees'-wax, and one part of red ochre, by weight, melted together.

to each other. These junctions bore a pressure of thirty, forty, and fifty atmospheres, with only one failure, in above one hundred instances; and that produced no complete separation of parts, but simply a small leak.

The caps, stop-cocks, and connectors, screwed one into the other, having one common screw thread, so as to be combined in any necessary manner. There were also screw plugs, some solid, with a male screw to close the openings or ends of caps, &c., others with a female screw to cover and close the ends of stop-cocks. All these screw joints were made tight by leaden washers; and by having these of different thickness, equal to from $\frac{4}{8}$th to $\frac{12}{8}$th of the distance between one turn of the screw thread and the next, it was easy at once to select the washer which should allow a sufficient compression in screwing up to make all air-tight, and also bring every part of the apparatus into its right position.

I have often put a pressure of fifty atmospheres into these tubes, and have had no accident or failure (except the one mentioned). With the assistance of Mr. ADDAMS I have tried their strength by a hydrostatic press, and obtained the following results:—A tube having an external diameter of 0.24 of an inch and a thickness of 0.0175 of an inch, burst with a pressure of sixty-seven atmospheres, reckoning one atmosphere as 15 lb. on the square inch. A tube which had been used, of the shape of fig. 1, its external diameter being 0.225 of an inch, and its thickness about 0.03 of an inch, sustained a pressure of 118 atmospheres without breaking, or any failure of the caps or cement, and was then removed for further use.

A tube such as I have employed for generating gases under pressure, having an external diameter of 0.6 of an inch, and a thickness of 0.035 of an inch, burst at twenty-five atmospheres.

Having these data, it was easy to select tubes abundantly sufficient in strength to sustain any force which was likely to be exerted within them in any given experiment.

The gauge used to estimate the degree of pressure to which the gas within the condensing tube was subjected was of the same kind as those formerly described,* being a small tube of glass closed at one end with a cylinder of mercury moving in it. So the expression of ten or twenty atmospheres, means a force which is able to compress a given portion of air into $\frac{1}{10}$th or $\frac{1}{20}$th of its bulk at the pressure of one atmosphere of thirty inches of mercury. These gauges had their graduation marked on them with a black varnish, and also with Indian ink:—there are several of the gases which, when condensed, cause the varnish to liquefy, but then the Indian ink stood. For further precaution, an exact copy of the gauge was taken on paper, to be applied on the outside of the condensing tube. In most cases, when the experiment was over, the pressure was removed from the interior of the apparatus, to ascertain whether the mercury in the gauge would return back to its first or starting-place.

For the application of cold to these tubes a bath of THILORIER'S mixture of solid carbonic acid and ether was used. An earthenware dish of the capacity of four cubic inches or more was fitted into a similar dish somewhat larger, with three or four folds of dry flannel intervening, and then the bath mixture was made in the inner dish. Such a bath will easily continue for twenty or thirty minutes, retaining solid carbonic acid the whole time; and the glass tubes used would sustain sudden immersion in it without breaking.

But as my hopes of any success beyond that heretofore obtained depended more upon depression of temperature than on the pressure which I could employ in these tubes, I endeavoured to obtain a still greater degree of cold. There are, in fact, some results producible by cold which no pressure may be able to effect. Thus, solidification has not as yet been conferred on a fluid by any degree of pressure. Again, that beautiful condition which CAGNIARD DE LA TOUR has made known, and which comes on with liquids at a certain heat, may have its point of temperature for some of the bodies to be experimented with, as oxygen, hydrogen, nitrogen, &c., below that belonging to the bath of carbonic acid and ether ; and, in that case, no pressure which any apparatus could bear would be able to bring them into the liquid or solid state.

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* Philosophical Transactions, 1823, p. 192.

To procure this lower degree of cold, the bath of carbonic acid and ether was put into an air-pump, and the air and gaseous carbonic acid rapidly removed. In this way the temperature fell so low, that the vapour of carbonic acid given off by the bath, instead of having a pressure of one atmosphere, had only a pressure of $\frac{1}{24}$th of an atmosphere, or 1.2 inch of mercury; for the air-pump barometer could be kept at 28.2 inches when the ordinary barometer was at 29.4. At this low temperature the carbonic acid mixed with the ether was not more volatile than water at the temperature of 86°, or alcohol at ordinary temperatures.

In order to obtain some idea of this temperature, I had an alcohol thermometer made, of which the graduation was carried below 32° FAHR., by degrees equal in capacity to those between 32° and 212°. When this thermometer was put into the bath of carbonic acid and ether surrounded by the air, but covered over with paper, it gave the temperature of 106° below 0°. When it was introduced into the bath under the air-pump, it sank to the temperature of 166° below 0°; or 60° below the temperature of the same bath at the pressure of one atmosphere, *i.e.* in the air. In this state the ether was very fluid, and the bath could be kept in good order for a quarter of an hour at a time.

As the exhaustion proceeded I observed the temperature of the bath and the corresponding pressure, at certain other points, of which the following may be recorded:— The external barometer was 29.4 inches:

	inch.		FAHR. °
when the mercury in the air-pump barometer was	1	the bath temperature was	—106,
... ...	10	... ...	—112½,
... ...	20	... ...	—121,
... ...	22	... ...	—125,
... ...	24	... ...	—131,
... ...	26	... ...	—139,
... ...	27	... ...	—146,
... ...	28	... ...	—160,
... ...	28.2	... ...	—166,

but as the thermometer takes some time to acquire the temperature of the bath, and the latter was continually falling in degree; as also the alcohol thickens considerably at the lower temperature, there is no doubt that the degrees expressed are not so low as they ought to be, perhaps even by 5° or 6° in most cases.

With *dry* carbonic acid under the air-pump receiver I could raise the pump barometer to twenty-nine inches when the external barometer was at thirty inches.

The arrangement by which this cooling power was combined in its effect on gases with the pressure of the pumps, was very simple in principle. An air-pump receiver open at the top was employed; the brass plate which closed the aperture had a small brass tube about six inches long, passing through it air-tight by means of a stuffing-box, so as to move easily up and down in a vertical direction. One of the glass condensing siphon tubes, already described, fig. 1, was screwed on to the lower end of the sliding tube, and the upper end of the latter was connected with a communicating tube in two lengths, reaching from it to the condensing pumps ; this tube was small, of brass, and 9½ feet in length ; it passed six inches horizontally from the condensing pumps, then rose vertically for two feet, afterwards proceeded horizontally for seven feet, and finally turned down and was immediately connected with the sliding tube. By this means the latter could be raised and lowered vertically, without any strain upon the connections, and the condensing tube lowered into the cold bath *in vacuo*, or raised to have its contents examined at pleasure. The capacity of the connecting tubes beyond the last condensing pump was only two cubic inches.

When experimenting with any particular gas, the apparatus was put together fast and tight, except the solid terminal screw-plug at the short end of the condensing tube, which being the very extremity of the apparatus, was left a little loose. Then, by the condensing pumps, abundance of gas was passed through the apparatus to sweep out every portion of air, after which the terminal plug was screwed up, the cold bath arranged, and the combined effects of cold and pressure brought to unite upon the gas.

There are many gases which condense at less than the pressure of one atmosphere when submitted to the cold of a carbonic acid bath in air (which latter can upon occasions be brought considerably below —106° FAHR.). These it was easy, therefore, to reduce, by sending them through small conducting tubes into tubular receivers placed in the cold bath. When the receivers had previously been softened in a spirit lamp flame, and narrow necks formed on them, it was not difficult by a little further management, hermetically to seal up these substances in their condensed state. In this manner chlorine, cyanogen, ammonia, sulphuretted hydrogen, arseniuretted hydrogen, hydriodic acid, hydrobromic acid, and even carbonic acid, were obtained, sealed up in tubes in the liquid state; and euchlorine was also secured in a tube receiver with a cap and screw-plug. By using a carbonic acid bath, first cooled *in vacuo*, there is no doubt other condensed gases could be secured in the same way.

The fluid carbonic acid was supplied to me by Mr. ADDAMS, in his perfect apparatus, in portions of about 220 cubic inches each. The solid carbonic acid, when produced from it, was preserved in a glass; itself retained in the middle of three concentric glass jars, separated from each other by dry jackets of woollen cloth. So effectual was this arrangement, that I have frequently worked for a whole day of twelve and fourteen hours, having solid carbonic acid in the reservoir, and enough for all the baths I required during the whole time, produced by one supply of 220 cubic inches.*

By the apparatus, and in the manner, now described, all the gases before condensed were very easily reduced, and some new results were obtained. When a gas was liquefied, it was easy to close the stop-cock, and then remove the condensing tube with the fluid from the rest of the apparatus. But in order to preserve the liquid from escaping as gas, a further precaution was necessary; namely, to cover over the exposed end of the stop-cock by a blank female screw-cap and leaden washer, and also to tighten perfectly the screw of the stop-cock plug. With these precautions I have kept carbonic acid, nitrous oxide, fluosilicon, &c., for several days.

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* On one occasion the solid carbonic acid was exceedingly electric, but I could not produce the effect again: it was probably connected with the presence of oil which was in the carbonic acid box; neither it nor the filaments of ice which formed on it in the air conducted, for when touched it preserved its electric state. Believing as yet that the account I have given of the cause of the electric state of an issuing jet of steam and water (Phil. Trans. 1843, p. 17) is the true one, I conclude that this also was a case of the production of electricity simply by friction, and unconnected with vaporization.

Even with gases which could be condensed by the carbonic acid bath in air, this apparatus in the air-pump had, in one respect, the advantage; for when the condensing tube was lifted out of the bath into the air, it immediately became covered with hoar frost, obscuring the view of that which was within; but *in vacuo* this was not the case, and the contents of the tube could be very well examined by the eye.

Olefiant gas.—This gas condensed into a clear, colourless, transparent fluid, but did not become solid even in the carbonic acid bath *in vacuo;* whether this was because the temperature was not low enough, or for other reasons referred to in the account of euchlorine, is uncertain.

The pressure of the vapour of this substance at the temperature of the carbonic acid bath in air (−103° FAHR.) appeared singularly uncertain, being on different occasions, and with different specimens, 3.7, 8.7, 5 and 6 atmospheres. The Table below shows the tension of vapour for certain degrees below 0° FAHR., with two different specimens obtained at different times, and it will illustrate this point.

FAHR. °	Atmospheres.	Atmospheres.
—100	4.60	9.30
— 90	5.68	10.26
— 80	6.92	11.33
— 70	8.32	12.52
— 60	9.88	13.86
— 50	11.72	15.36
— 40	13.94	17.05
— 30	16.56	18.98
— 20	19.58	21.23
— 10	. .	23.89
0	. .	27.18
10	. .	31.70
20	. .	36.80
30	. .	42.50

I have not yet resolved this irregularity, but believe there are two or more substances, physically, and perhaps occasionally chemically different, in olefiant gas; and varying in proportion with the circumstances of heat, proportions of ingredients, &c., attending the preparation.

The fluid affected the resin of the gauge graduation, and probably also the resin of the cap cement, though slowly.

Hydriodic acid.—This substance was prepared from the iodide of phosphorus by heating it with a very little water. It is easily condensable by the temperature of a carbonic acid bath; it was redistilled, and thus obtained perfectly pure.

The acid may be obtained either in the solid or liquid, or (of course) in the gaseous state. As a solid it is perfectly clear, transparent, and colourless; having fissures or cracks in it resembling those that run through ice. Its solidifying temperature is nearly —60° FAHR., and then its vapour has not the pressure of one atmosphere; at a point a little higher it becomes a clear liquid, and this point is close upon that which corresponds to a vaporous pressure of one atmosphere. The acid dissolves the cap cement and the bitumen of the gauge graduation; and appears also to dissolve and act on fat, for it leaked by the plug of the stop-cock with remarkable facility. It acts on the brass of the apparatus, and also on the mercury in the gauge. Hence the following results as to pressures and temperatures are not to be considered more than approximations :—

At 0° FAHR. pressure was 2.9 atmospheres.
At 32° FAHR. pressure was 3.97 atmospheres.
At 60° FAHR. pressure was 5.86 atmospheres.

Hydrobromic acid.—This acid was prepared by adding to perbromide of phosphorus* about one-third of its bulk of water in a proper distillatory apparatus formed of glass tube, and then applying heat to distil off the gaseous acid. This being sent into a very cold receiver, was condensed into a liquid, which being rectified by a second distillation, was then experimented with.

Hydrobromic acid condenses into a clear colourless liquid at 100° below 0°, or lower, and has not the pressure of one atmosphere at the temperature of the carbonic acid bath in air. It soon obstructs and renders the motion of the mercury in the air-gauge irregular, so that I did not obtain a measure of its elastic force; but it is less than that of muriatic acid. At and below the temperature of —124° FAHR. it is a solid, transparent, crystalline body. It does not freeze until reduced much lower than this temperature; but being frozen by the carbonic acid bath *in vacuo*, it remains a solid until the temperature in rising attains to —124°.

Fluosilicon.—I found that this substance in the gaseous state might be brought in contact with the oil and metal of the pumps, without causing injury to them, for a time sufficiently long to apply the joint process of condensation already described. The substance liquefied under a pressure of about nine atmospheres at the lowest temperature, or at 160° below 0°; and was then clear, transparent, colourless, and very fluid like hot ether. It did not solidify at any temperature to which I could submit it. I was able to preserve it in the tube until the next day. Some leakage had then taken place (for it ultimately acted on the lubricating fat of the stop-cock), and there was no liquid in the tube at common temperatures; but when the bend of the tube was cooled to 32° by a little ice, fluid appeared: a bath of ice and salt caused a still more abundant condensation. The pressure appeared then to be above thirty atmospheres, but the motion of the mercury in the gauge had become obstructed through the action of the fluosilicon, and no confidence could be reposed in its indications.

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* The bromides of phosphorus are easily made without risk of explosion. If a glass tube be bent so as to have two depressions, phosphorus placed in one and bromine in the other; then by inclining the tube, the vapour of bromine can be made to flow gradually on to, and combine with, the phosphorus. The fluid protobromide is first formed, and this is afterwards converted into solid perbromide. The excess of bromine may be dissipated by the careful application of heat.

Phosphuretted hydrogen.—This gas was prepared by boiling phosphorus in a strong pure solution of caustic potassa, and the gas was preserved over water in a dark room for several days to cause the deposition of any mere vapour of phosphorus which it might contain. It was then subjected to high pressure in a tube cooled by a carbonic acid bath, which had itself been cooled under the receiver of the air-pump. The gas in its way to the pumps passed through a long spiral of thin narrow glass tube immersed in a mixture of ice and salt at 0°, to remove as much water from it as possible.

By these means the phosphuretted hydrogen was liquefied; for a pure, clear, colourless, transparent and very limpid fluid appeared, which could not be solidified by any temperature applied, and which when the pressure was taken off immediately rose again in the form of gas. Still the whole of the gas was not condensable into this fluid. By working the pumps the pressure would rise up to twenty-five atmospheres at this very low temperature, and yet at the pressure of two or three atmospheres and the same temperature, liquid would remain. There can be no doubt that phosphuretted hydrogen condensed, but neither can there be a doubt that some other gas, not so condensable, was also present, which perhaps may be either another phosphuretted hydrogen or hydrogen itself.

Fluoboron.—This substance was prepared from fluor spar, fused boracic acid and strong sulphuric acid, in a tube generator such as that already described, and conducted into a condensing tube under the generating pressure. The ordinary carbonic acid bath did not condense it, but the application of one cooled under the air-pump caused its liquefaction, and fluoboron then appeared as a very limpid, colourless, clear fluid, showing no signs of solidification, but when at the lowest temperature mobile as hot ether. When the pressure was taken off, or the temperature raised, it returned into the state of gas.

The following are some results of pressure, all that I could obtain with the liquid in my possession; for, as the liquid is light and the gas heavy, the former rapidly disappears in producing the latter. They make no pretensions to accuracy, and are given only for general information.

FAHR. °	Atmospheres.	FAHR. °	Atmospheres.	FAHR. °	Atmospheres.
—100	4.61	—72	9.23	—62	11.54
— 82	7.5	—66	10.00		

The preceding are, as far as I am aware, new results of the liquefaction and solidification of gases. I will now briefly add such other information respecting solidification, pressure, &c., as I have obtained with gaseous bodies previously condensed. As to pressure, considerable irregularity often occurred, which I cannot always refer to its true cause; sometimes a little of the compressed gas would creep by the mercury in the gauge, and increase the volume of inclosed air; and this varied with different substances, probably by some tendency which the glass had to favour the condensation of one (by something analogous to hygrometric action) more than another. But even when the mercury returned to its place in the gauge, there were anomalies which seemed to imply, that a substance, supposed to be one, might be a mixture of two or more. It is, of course, essential that the gauge be preserved at the same temperature throughout the observations.

Muriatic acid.—This substance did not freeze at the lowest temperature to which I could attain. Liquid muriatic acid dissolves bitumen; the solution, liberated from pressure, boils, giving off muriatic acid vapour, and the bitumen is left in a solid frothy state, and probably altered, in some degree, chemically. The acid unites with and softens the resinous cap cement, but leaves it when the pressure is diminished. The following are certain pressures and temperatures which, I believe, are not very far from truth; the marked numbers are from experiment.

FAHR. °	Atmospheres.	FAHR. °	Atmospheres.	FAHR. °	Atmospheres.
⌣—100	1.80	⌣—53	5.83	⌣— 5	13.88
⌣— 92	2.28	—50	6.30	⌣ 0	15.04
— 90	2.38	⌣—42	7.40	10	17.74
⌣— 83	2.90	—40	7.68	20	21.09
— 80	3.12	⌣—33	8.53	⌣ 25	23.08
⌣— 77	3.37	—30	9.22	30	25.32
— 70	4.02	⌣—22	10.66	⌣ 32	26.20
⌣— 67	4.26	—20	10.92	40	30.67
— 60	5.08	—10	12.82		

The result formerly obtained* was forty atmospheres at the temperature of 50° FAHR.

Sulphurous acid.—When liquid, it dissolves bitumen. It becomes a crystalline, transparent, colourless, solid body, at —105° FAHR.; when partly frozen the crystals are well-formed. The solid sulphurous acid is heavier than the liquid, and sinks freely in it. The following is a table of pressures in atmospheres of 30 inches mercury, of which the marked results are from many observations, the others are interpolated. They differ considerably from the results obtained by Bunsen,[*] but agree with my first and only result.

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* Philosophical Transactions, 1823, p. 198.

Fahr. °	Atmospheres.	Fahr. °	Atmospheres.	Fahr. °	Atmospheres
0	0.725	40	1.78	76·8	3.50
10	0.92	46.5	2.00	85	4.00
⌣14	1.00	⌣48	2.06	⌣90	4.35
⌣19	1.12	⌣56	2.42	93	4.50
⌣23	1.23	58	2.50	98	5.00
⌣26	1.33	⌣64	2.76	⌣100	5.16
31.5	1.50	68	3.00	104	5.50
⌣32	1.53	⌣73.5	3.28	110	6.00
⌣33	1.57				

Sulphuretted hydrogen.—This substance solidifies at 122° Fahr. below 0°, and is then a white crystalline translucent substance, not remaining clear and transparent in the solid state like water, carbonic acid, nitrous oxide, &c., but forming a mass of confused crystals like common salt or nitrate of ammonia, solidified from the melted state. As it fuses at temperatures above —122°, the solid part sinks freely in the fluid, indicating that it is considerably heavier. At this temperature the pressure of its vapour is less than one atmosphere, not more, probably, than 0.8 of an atmosphere, so that the liquid allowed to evaporate in the air would not solidify as carbonic acid does.

The following is a table of the tension of its vapour, the marked numbers being close to experimental results, and the rest interpolated. The curve resulting from these numbers, though coming out nearly identical in different series of experiments, is apparently so different in its character from that of water or carbonic acid, as to leave doubts on my mind respecting it, or else of the identity of every portion of the fluid obtained, yet the crystallization and other characters of the latter seemed to show that it was a pure substance.

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[*] Bibliothèque Universelle, 1839, xxiii. p. 185.

Fahr. °	Atmospheres.	Fahr. °	Atmospheres.	Fahr. °	Atmospheres.
—100	1.02	—50	2.35	0	6.10
— 94	1.09	—45	2.59	10	7.21
— 90	1.15	—40	2.86	20	8.44
— 83	1.27	—30	3.49	26	9.36
— 80	1.33	—24	3.95	30	9.94
— 74	1.50	—20	4.24	40	11.84
— 70	1.59	—16	4.60	48	13.70
— 68	1.67	—10	5.11	50	14.14
— 60	1.93	— 2	5.90	52	14.60
— 58	2.00				

Carbonic acid.—The solidification of carbonic acid by M. Thilorier is one of the most beautiful experimental results of modern times. He obtained the substance, as is well known, in the form of a concrete white mass like fine snow, aggregated. When it is melted and resolidified by a bath of low temperature, it then appears as a clear, transparent, crystalline, colourless body, like ice; so clear, indeed, that at times it was doubtful to the eye whether anything was in the tube, yet at the same time the part was filled with solid carbonic acid. It melts at the temperature of —70° or —72° Fahr., and the solid carbonic acid is heavier than the fluid bathing it. The solid or liquid carbonic acid at this temperature has a pressure of 5.33 atmospheres nearly. Hence it is easy to understand the readiness with which liquid carbonic acid, when allowed to escape into the air, exerting only a pressure of one atmosphere, freezes a part of itself by the evaporation of another part.

Thilorier gives —100° C. or —148° Fahr. as the temperature at which carbonic acid becomes solid. This however is rather the temperature to which solid carbonic acid can sink by further evaporation in the air, and is a temperature belonging to a pressure, not only lower than that of 5.33 atmospheres, but even much below that of one atmosphere. This cooling effect to temperatures below the boiling-point often appears. A bath of carbonic acid and ether exposed to the air will cool a tube containing condensed solid carbonic acid, until the pressure within the tube is less than one atmosphere; yet, if the same bath be covered up so as to have the pressure of one atmosphere of carbonic acid vapour over it, then the temperature is such as to produce a pressure of 2.5 atmospheres by the vapour of the solid carbonic acid within the tube.

The estimates of the pressure of carbonic acid vapour are sadly at variance; thus, THILORIER* says it has a pressure of 26 atmospheres at —4° FAHR., whilst ADDAMS† says that for that pressure it requires a temperature of 30°. ADDAMS gives the pressure about 27½ atmospheres at 32°, but THILORIER and myself‡ give it as 36 atmospheres at the same temperature. At 50° BRUNEL§ estimates the pressure as 60 atmospheres, whilst ADDAMS makes it only 34.67 atmospheres. At 86° THILORIER finds the pressure to be 73 atmospheres; at 4° more, or 90°, BRUNEL makes it 120 atmospheres; and at 10° more, or 100°, ADDAMS makes it less than THILORIER at 86°, and only 62.32 atmospheres; even at 150° the pressure with him is not quite 100 atmospheres.

I am inclined to think that at about 90° CAGNIARD DE LA TOUR'S state comes on with carbonic acid. From THILORIER'S data we may obtain the specific gravity of the liquid and the vapour over it at the temperature of 86° FAHR., and the former is little more than twice that of the latter; hence a few degrees more of temperature would bring them together, and BRUNEL's result seems to imply that the state was then on, but in that case ADDAMS's results could only be accounted for by supposing that there was a deficiency of carbonic acid. The following are the pressures which I have recently obtained :—

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* Annales de Chimie, 1835, lx. 427, 432.

† Report of British Association, 1838, p. 70.

‡ Philosophical Transactions, 1823, p. 193.

§ Royal Institution Journal, xxi. 132.

FAHR. °	Atmospheres.	FAHR. °	Atmospheres.	FAHR. °	Atmospheres
—111	1.14	—60	6.97	— 4	21.48
—110	1.17	—56	7.70	0	22.84
—107	1.36	—50	8.88	5	24.75
—100	1.85	—40	11.07	10	26.82
— 95	2.28	—34	12.50	15	29.09
— 90	2.77	—30	13.54	20	30.65
— 83	3.60	—23	15.45	23	33.15
— 80	3.93	—20	16.30	30	37.19
— 75	4.60	—15	17.80	32	38.50
— 70	5.33	—10	19.38		

Carbonic acid is remarkable amongst bodies for the high tension of the vapour which it gives off whilst in the solid or glacial state. There is no other substance which at all comes near it in this respect, and it causes an inversion of what in all other cases is the natural order of events. Thus, if, as is the case with water, ether, mercury or any other fluid, that temperature at which carbonic acid gives off vapour equal in elastic force to one atmosphere, be called its boiling-point ; or, if (to produce the actual effect of ebullition) the carbonic acid be plunged below the surface of alcohol or ether, then we shall perceive that the freezing and boiling-points are inverted, i.e. that the freezing-point is the hotter, and the boiling-point the colder of the two, the latter being about 50° below the former.

Euchlorine. — This substance was easily converted from the gaseous state into a solid crystalline body, which, by a little increase of temperature, melted into an orange-red fluid, and by diminution of temperature again congealed ; the solid euchlorine had the colour and general appearance of bichromate of potassa; it was moderately hard, brittle and translucent; and the crystals were perfectly clear. It melted at the temperature of 75° below 0°, and the solid portion was heavier than the liquid.

When in the solid state it gives off so little vapour that the eye is not sensible of its presence by any degree of colour in the air over it when looking down a tube four inches in length, at the bottom of which is the substance. Hence the pressure of its vapour at that temperature must be very small.

Some hours after, wishing to solidify the same portion of euchlorine which was then in a liquid state, I placed the tube in a bath at —110°, but could not succeed either by continuance of the tube in the bath, or shaking the fluid in the tube, or opening the tube to allow the full pressure of the atmosphere; but when the liquid euchlorine was touched by a platinum wire it instantly became solid, and exhibited all the properties before described. There are many similar instances amongst ordinary substances, but the effect in this case makes me hesitate in concluding that all the gases which as yet have refused to solidify at temperatures as low as 166° below 0°, cannot acquire the solid state at such a temperature.

Nitrous oxide.—This substance was obtained *solid* by the temperature of the carbonic acid bath *in vacuo*, and appeared as a beautiful clear crystalline colourless body. The temperature required for this effect must have been very nearly the lowest, perhaps about 150° below 0°. The pressure of the vapour rising from the solid nitrous oxide was less than one atmosphere.

Hence it was concluded that liquid nitrous oxide could not freeze itself by evaporation at one atmosphere, as carbonic acid does; and this was found to be true, for when a tube containing much liquid was freely opened, so as to allow evaporation down to one atmosphere, the liquid boiled and cooled itself, but remained a liquid. The cold produced by the evaporation was very great, and this was shown by putting the part of the tube containing the liquid nitrous oxide, into a cold bath of carbonic acid, for the latter was like a hot bath to the former, and instantly made it boil rapidly.

I kept this substance for some weeks in a tube closed by stop-cocks and cemented caps. In that time there was no action on the bitumen of the graduation, nor on the cement of the caps; these bodies remained perfectly unaltered.

Hence it is probable that this substance may be used in certain cases, instead of carbonic acid, to produce degrees of cold far below those which the latter body can supply. Down to a certain temperature, that of its solidification, it would not even require ether to give contact, and below that temperature it could easily be used mingled with ether; its vapour would do no harm to an air-pump, and there is no doubt that the substance placed *in vacuo* would acquire a temperature lower than any as yet known, perhaps as far below the carbonic acid bath *in vacuo* as that is below the same bath in air.

This substance, like olefiant gas, gave very uncertain results at different times as to the pressure of its vapour; results which can only be accounted for by supposing that there are two different bodies present, soluble in each other, but differing in the elasticity of their vapour. Four different portions gave at the same temperature, namely, —106° FAHR., the following great differences in pressure, 1.66; 4.4; 5.0; and 6.3 atmospheres, and this after the elastic atmosphere left in the tubes at the conclusion of the condensation had been allowed to escape, and be replaced by a portion of the respective liquids which then rose in vapour. The following Table gives certain results with a portion of liquid which exerted a pressure of six atmospheres at —106° FAHR.

FAHR. °	Atmospheres.	Atmospheres.
—40	10.20	
—35	10.95	
—30	11.80	
—25	12.75	
—20	13.80	
—15	14.95	
—10	16.20	
— 5	17.55	
0	19.05	24.40
5	20.70	26.08
10	22.50	27.84
15	24.45	29.68
20	26.55	31.62
25	28.85	33.66
30		35.82
35		38.10

The second column expresses the pressures given as the fluid was raised from low to higher temperatures. The third column shows the pressures given the next day with the same tube after it had attained to and continued at the atmospheric temperature for some hours. There is a difference of four or five atmospheres between the two, showing that in the first instance the previous low temperature had caused the solution of a more volatile part in the less volatile and liquid portion, and that the prolonged application of a higher temperature during the night had gradually raised it again in vapour. This result occurred again and again with the same specimen.*

Cyanogen. — This substance becomes a solid transparent crystalline body, as BUNSEN has already stated,[*] which raised to the temperature of —30° FAHR. then liquefies. The solid and liquid appear to be nearly of the same specific gravity, but the solid is perhaps the denser of the two.

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* This substance is one of those which I liquefied in 1823 (see Philosophical Transactions). Since writing the above I perceive that M. NATTERER has condensed it into the liquid state by the use of pumps only (see Comptes Rendus, 1844, 18th Nov. p. 1111), and obtained the liquid in considerable quantities. The non-solidification of it by exposure to the air perfectly accords with my own results.

The mixed solid and liquid substance yields a vapour of rather less pressure than one atmosphere. In accordance with this result, if the liquid be exposed to the air, it does not freeze itself as carbonic acid does.

The liquid tends to distil over and condense on the cap cement and bitumen of the gauge, but only slightly. When cyanogen is made from cyanide of mercury sealed up hermetically in a glass tube, the cyanogen distils back and condenses in the paracyanic residue of the distillation, but the pressure of the vapour at common temperatures is still as great, or very nearly so, as if the cyanogen were in a clean separate liquid state.

A measured portion of liquid cyanogen was allowed to escape and expand into gas. In this way one volume of liquid at the temperature of 63° FAHR. gave 393.9 volumes of gas at the same temperature and the barometric pressure of 30.2 inches. If 100 cubic inches of the gas be admitted to weigh 55.5 grains, then a cubic inch of the liquid would weigh 218.6 grains. This gives its specific gravity as 0.866. When first condensed I estimated it as nearly 0.9.

Cyanogen is a substance which yielded on different occasions results of vaporous tension differing much from each other, though the substance appeared always to be pure. The following are numbers in which I place some confidence, the pressures being in atmospheres of 30 inches of mercury, and the marked results experimental.[†]

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[*] Bibliothèque Universelle, 1839, xxiii. p. 184.

[†] See BUNSEN's results, Bibliothèque Universelle, 1839, xxiii. p. 185.

Fahr. °	Atmospheres.	Fahr. °	Atmospheres.	Fahr. °	Atmospheres.
0	1.25	◡38.5	2.72	77	5.00
8.5	1.5	◡44.5	3.00	◡79	5.16
◡10	1.53	◡48	3.17	83	5.50
15	1.72	◡50	3.28	88.3	6.00
◡20	1.89	◡52	3.36	◡93.5	6.50
22.8	2.00	54.3	3.50	◡95	6.64
◡27	2.20	◡63	4.00	98.4	7.00
◡32	2.37	◡70	4.50	◡103	7.50
34.5	2.50	◡74	4.79		

Ammonia.—This body may be obtained as a *solid*, white, translucent, crystalline substance, melting at the temperature of 103° below 0°; at which point the solid substance is heavier than the liquid. In that state the pressure of its vapour must be very small.

Liquid ammonia at 60° was allowed to expand into ammoniacal gas at the same temperature; one volume of the liquid gave 1009.8 volumes of the gas, the barometer being at the pressure of 30.2 inches. If 100 cubic inches of ammoniacal gas be allowed to weigh 18.28 grains, it will give 184.6 grains as the weight of a cubic inch of liquid ammonia at 60°. Hence its specific gravity at that temperature will be 0.731. In the old experiments I found by another kind of process that its specific gravity was 0.76 at 50°.

The following is a table of the pressure of ammonia vapour, the marked results, as before, being those obtained by experiment:—

Fahr. °	Atmospheres.	Fahr. °	Atmospheres.	Fahr. °	Atmospheres.
◡0	2.48	◡41	5.10	◡61.3	7.00
0.5	2.50	◡44	5.36	◡65.6	7.50
◡9.3	3.00	◡45	5.45	◡67	7.63
◡18	3.50	45.8	5.50	69.4	8.00
◡21	3.72	◡49	5.83	73	8.50
25.8	4.00	◡51.4	6.00	76.8	9.00
◡26	4.04	◡52	6.10	80	9.50
◡32	4.44	◡55	6.38	◡83	10.00
◡33	4.50	◡56.5	6.50	85	10.30
39.5	5.00	◡60	6.90		

Arseniuretted Hydrogen.—This body, liquefied by Dumas and Soubeiran, did not solidify at the lowest temperature to which I could submit it, i.e. not at 166° below 0° Fahr. In the following table of the elasticity of its vapour the marked results are experimental, and the others interpolated:—

Fahr. °	Atmospheres.	Fahr. °	Atmospheres.	Fahr. °	Atmospheres.
◡—75	0.94	—30	2.84	◡10	6.24
—70	1.08	◡—23	3.32	◡20	7.39
◡—64	1.26	—20	3.51	30	8.66
—60	1.40	—10	4.30	◡32	8.95
◡—52	1.73	◡— 5	4.74	◡40	10.05
—50	1.80	◡ 0	5.21	◡50	11.56
—40	2.28	◡ 3	5.56	◡60	13.19
◡—36	2.50				

The following bodies would not freeze at the very low temperature of the carbonic acid bath *in vacuo* (—166° Fahr.):—Chlorine, ether, alcohol, sulphuret of carbon, caoutchoucine, camphine or rectified oil of turpentine. The alcohol, caoutchoucine, and camphine lost fluidity and thickened somewhat at —106°, and still more at the lower temperature of —166°. The alcohol then poured from side to side like an oil.

Dry yellow fluid nitrous acid when cooled below 0° loses the greater part of its colour, and then fuses into a white, crystalline, brittle and but slightly translucent substance, which fuses a little above 0° Fahr. The green and probably hydrated acid required a much lower temperature for its solidification, and then became a pale bluish solid. There were then evidently two bodies, the dry acid which froze out first, and then the hydrate, which requires at least —30° below 0° before it will solidify.

The following gases showed no signs of liquefaction when cooled by the carbonic acid bath *in vacuo*, even at the pressures expressed :—

	Atmospheres.
Hydrogen at	27
Oxygen at	27
Nitrogen at	50
Nitric oxide at	50
Carbonic oxide at	40
Coal gas	32

The difference in the facility of leakage was one reason of the difference in the pressure applied. I found it impossible, from this cause, to raise the pressure of hydrogen higher than twenty-seven atmospheres by an apparatus that was quite tight enough to confine nitrogen up to double that pressure.

M. CAGNIARD DE LA TOUR has shown that at a certain temperature, a liquid, under sufficient pressure, becomes clear transparent vapour or gas, having the same bulk as the liquid. At this temperature, or one a little higher, it is not likely that any increase of pressure, except perhaps one exceedingly great, would convert the gas into a liquid. Now the temperature of 166° below 0°, low as it is, is probably *above* this point of temperature for hydrogen, and perhaps for nitrogen and oxygen, and then no compression without the conjoint application of a degree of cold below that we have as yet obtained, can be expected to take from them their gaseous state. Further, as ether assumes this state before the pressure of its vapour has acquired thirty-eight atmospheres, it is more than probable that gases which can resist the pressure of from twenty-seven to fifty atmospheres at a temperature of 166° below 0° could never appear as liquids, or be made to lose their gaseous state at common temperatures. They may probably be brought into the state of very condensed gases, but not liquefied.

Some very interesting experiments on the compression of gases have been made by M. G. AIME,* in which oxygen, olefiant, nitric oxide, carbonic oxide, fluosilicon, hydrogen, and nitrogen gases were submitted to pressures, rising up to 220 atmospheres in the case of the two last; but this was in the depths of the sea where the results under pressure could not be examined. Several of them were diminished in bulk in a ratio far greater than the pressure put upon them; but both M. CAGNIARD DE LA TOUR and M. THILORIER have shown that this is often the case whilst the substance retains the gaseous form. It is possible that olefiant gas and fluosilicon may have liquefied down below, but they have not yet been seen in the liquid state except in my own experiments, and in them not at temperatures above 40° FAHR. The results with oxygen are so unsteady and contradictory as to cause doubt in regard to those obtained with the other gases by the same process.

Thus, though as yet I have not condensed oxygen, hydrogen, or nitrogen, the original objects of my pursuit, I have added six substances, usually gaseous, to the list of those that could previously be shown in the liquid state, and have reduced seven, including ammonia, nitrous oxide, and sulphuretted hydrogen, into the solid form. And though the numbers expressing tension of vapour cannot (because of the difficulties respecting the use of thermometers and the apparatus generally) be considered as exact, I am in hopes they will assist in developing some general law governing the vaporization of all bodies, and also in illustrating the physical state of gaseous bodies as they are presented to us under ordinary temperature and pressure.

Royal Institution,
Nov. 15, 1844.

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* Annales de Chimie, 1843, viii. 275.

NOTE.—*Additional remarks respecting the Condensation of Gases.*

Received February 20,—*Read February* 20, 1845.

Nitrous oxide.—Suspecting the presence on former occasions of nitrogen in the nitrous oxide, and mainly because of muriate in the nitrate of ammonia used, I prepared that salt in a pure state from nitric acid and carbonate of ammonia previously proved, by nitrate of silver, to be free from muriatic acid. After the nitrous oxide prepared from this salt had remained for some days in well-closed bottles in contact with a little water, I condensed it in the manner already described, and when condensed I allowed half the fluid to escape in vapour, that as much as possible of the less condensable portion might be carried off. In this way as much gas as would fill the capacity of the vessels twenty or thirty times or more was allowed to escape. Afterwards the following series of pressures was obtained :—

FAHR. °	Atmospheres.	FAHR. °	Atmospheres.	FAHR. °	Atmospheres.
—125	1.00	—70	4.11	—15	14.69
—120	1.10	—65	4.70	—10	16.15
—115	1.22	—60	5.36	— 5	17.70
—110	1.37	—55	6.09	0	19.34
—105	1.55	—50	6.89	5	21.07
—100	1.77	—45	7.76	10	22.89
— 95	2.03	—40	8.71	15	24.80
— 90	2.34	—35	9.74	20	26.80
— 85	2.70	—30	10.85	25	28.90
— 80	3.11	—25	12.04	30	31.10
— 75	3.58	—20	13.32	35	33.40

These numbers may all be taken as the results of experiments. Where the temperatures are not those actually observed, they are in almost all cases within a degree of it, and proportionate to the effects really observed. The departure of the real observations from the numbers given is very small. This table I consider as far more worthy of confidence than the former, and yet it is manifest that the curve is not consistent with the idea of a pure single substance, for the pressures at the lowest temperature are too high. I believe that there are still two bodies present, and that the more volatile, as before said, is condensable in the liquid of the less volatile; but I think there is a far smaller proportion of the more volatile (nitrogen, or whatever it may be) than in the former case.

Olefiant gas.—The olefiant gas condensed in the former experiment was prepared in the ordinary way, using excellent alcohol and sulphuric acid; then washed by agitation with about half its bulk of water, and finally left for three days over a thick mixture of lime and water with occasional agitation. In this way all the sulphurous and carbonic acids were removed, and I believe all the ether, except such minute portions as could not interfere with my results. In respect of the ether, I have since found that the process is satisfactory; for when I purposely added ether vapour to air, so as to increase its bulk by one-third, treatment like that above removed it, so as to leave the air of its original volume. There was yet a slight odour of ether left, but not so much as that conferred by adding one volume of the vapour of ether to 1200 or 1500 volumes of air. I find that when air is expanded $\frac{1}{4}$th or $\frac{1}{3}$rd more by the addition of the vapour of ether, washing first of all with about $\frac{1}{10}$th of its volume of water, then again with about as much water, and lastly with its volume of water, removes the ether to such a degree, that though a little smell may remain, the air is of its original volume.

As already stated, it is the presence of other and more volatile hydrocarbons than olefiant gas, which the tensions obtained seemed to indicate, both in the gas and the liquid resulting from its condensation. In a further search after these I discovered a property of olefiant gas which I am not aware is known (since I do not find it referred to in books), namely its ready solubility in strong alcohol, ether, oil of turpentine, and such like bodies.* Alcohol will take up two volumes of this gas; ether can absorb two volumes; oil of turpentine two volumes and a half; and olive oil one volume by agitation at common temperatures and pressure; consequently, when a vessel of olefiant gas is transferred to a bath of any of these liquids and agitated, absorption quickly takes place.

Examined in this way, I have found no specimen of olefiant gas that is entirely absorbed; a residue always remains, which, though I have not yet had time to examine it accurately, appears to be light carburetted hydrogen; and I have no doubt that this is the substance which has mainly interfered in my former results. This substance appears to be produced in every stage of the preparation of olefiant gas. On taking six different portions of gas at different equal intervals, from first to last, during one process of preparation, after removing the sulphurous and carbonic acid and the ether as before described, then the following was the proportion per cent. of insoluble gas in the remainder when agitated with oil of turpentine, 10.5; 10; 10.1; 13.1; 28.3; 61.8. Whether carbonic oxide was present in any of these undissolved portions I cannot at present say.

In reference to the part dissolved, I wish as yet to guard myself from being supposed to assume that it is one uniform substance; there is indeed little doubt that the contrary is true; for whilst a volume of oil of turpentine introduced into twenty times its volume of olefiant gas cleared from ether and the acids, absorbs 2½ volumes of the gas, the same volume of fresh oil of turpentine brought into similar contact with abundance of the gas which remains when one-half has been removed by solution only dissolved 1.54 part, yet there was an abundant surplus of gas which would dissolve in fresh oil of turpentine at this latter rate. When two-thirds of a portion of fresh olefiant gas were removed by solution, the most soluble portion of that which remained required its bulk of fresh oil of turpentine to dissolve it. Hence at first one volume of camphine dissolved 2.50, but when the richer portion of the gas was removed, one volume dissolved 1.54 part; and when still more of the gas was taken away by solution, one volume of camphine dissolved only one volume of the gas. This can only be accounted for by the presence of various compounds in the soluble portion of the gas.

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* Water, as BERZELIUS and others have pointed out, dissolves about $\frac{1}{8}$th its volume of olefiant gas, but I find that it also leaves an insoluble residue, which burns like light carburetted hydrogen.

A portion of good olefiant gas was prepared, well-agitated with its bulk of water in close vessels, left over lime and water for three days, and then condensed as before. When much liquid was condensed, a considerable proportion was allowed to escape to sweep out the uncondensed atmosphere and the more condensable vapours; and then the following pressures were observed :—

Fahr. °	Atmospheres.	Fahr. °	Atmospheres.	Fahr. °	Atmospheres.
—105	4.60	—65	8.30	—30	16.22
—100	4.82	—60	9.14	—25	17.75
— 95	5.10	—55	10.07	—20	19.38
— 90	5.44	—50	11.10	—15	21.11
— 85	5.84	—45	12.23	—10	22.94
— 80	6.32	—40	13.46	— 5	24.87
— 75	6.89	—35	14.79	0	26.90
— 70	7.55				

On examining the form of the curve given by these pressures, it is very evident that, as on former occasions, the pressures at low temperatures are too great to allow the condensed liquid to be considered as one uniform body, and the form of the curve at the higher pressures is quite enough to prove that no ether was present either in this or the former fluids. On permitting the liquid in the tube to expand into gas, and treating 100 parts of that gas with oil of turpentine, eighty-nine parts were dissolved, and eleven parts remained insoluble. There can be no doubt that the presence of this latter substance, soluble as it is under pressure in the more condensable portions, is the cause of the irregularity of the curve, and the too high pressure at the lower temperatures.

The ethereal solution of olefiant gas being mixed with eight or nine times its volume of water, dissolved and gradually minute bubbles of gas appeared, the separation of which was hastened by a little heat. In this way about half the gas dissolved was re-obtained, and burnt like very rich olefiant gas. One volume of the alcoholic solution, with two volumes of water, gave very little appearance of separating gas. Even the application of heat did not at first cause the separation, but gradually about half the dissolved olefiant gas was liberated.

The separation of the dissolved gas by water, heat, or change of pressure from its solutions, will evidently supply means of procuring olefiant gas in a greater state of purity than heretofore; the power of forming these solutions will also very much assist in the correct analysis of mixtures of hydrocarbons. I find that light carburetted hydrogen is hardly sensibly soluble in alcohol or ether, and in oil of turpentine the proportion dissolved is not probably $\frac{1}{15}$th the volume of the fluid employed; but the further development of these points I must leave for the present.

Carbonic acid.—This liquid may be retained in glass tubes furnished with cemented caps, and closed by plugs or stop-cocks, as described, but it is important to remember the softening action on the cement which, being continued, at last reduces its strength below the necessary point. A tube of this kind was arranged on the 10th of January and left; on the 15th of February it exploded, not by any fracture of the tube, for that remained unbroken, but simply by throwing off the cap through a failure of the cement. Hence the cement joints should not be used for long experiments, but only for those enduring for a few days.

Oxygen.—Chlorate of potassa was melted and pulverized. Oxide of manganese was pulverized, heated red-hot for half an hour, mixed whilst hot with the chlorate, and the mixture put into a long strong glass generating tube with a cap cemented on, and this tube then attached to another with a gauge for condensation. The heat of a spirit lamp carefully applied produced the evolution of oxygen without any appearance of water, and the tubes, both hot and cold, sustained the force generated. In this manner the pressure of oxygen within the apparatus was raised as high as 58.5 atmospheres, whilst the temperature at the condensing place was reduced as low as —140° FAHR., but no condensation appeared. A little above this pressure the cement of two of the caps began to leak, and I could carry the observation no further with this apparatus.

From the former scanty and imperfect expressions of the elasticity of the vapour of the condensed gases, DOVE was led to put forth a suggestion,* whether it might not ultimately appear that the same addition of heat (expressed in degrees of the thermometer) caused the same additional increase of expansive force for all gases or vapours in contact with their liquids, provided the observation began with the same pressure in all. Thus to obtain the difference between forty-four and fifty atmospheres of pressure, either with steam or nitrous oxide, nearly the same number of degrees of heat were required; to obtain the difference between twenty and twenty-five atmospheres, either with steam or muriatic acid, the same number were required. Such a law would of course make the rate of increasing expansive force the same for all bodies, and the curve laid down for steam would apply to every other vapour. This, however, does not appear to be the case. That the force of the vapour increases in a geometrical ratio for equal increments of heat is true for all bodies, but the ratio is not the same for all. As far as observations upon the following substances, namely, water, sulphurous acid, cyanogen, ammonia, arseniuretted hydrogen, sulphuretted hydrogen, muriatic acid, carbonic acid, olefiant gas, &c., justify any conclusion respecting a general law, it would appear that the more volatile a body is, the more rapidly does the force of its vapour increase by further addition of heat, commencing at a given point of pressure for all; thus for an increase of pressure from two to six atmospheres, the following number of degrees require to be added for the different bodies named: water 69°, sulphurous acid 63°, cyanogen 64°.5, ammonia 60°, arseniuretted hydrogen 54°, sulphuretted hydrogen 56°.5, muriatic acid 43°, carbonic acid 32°.5, nitrous oxide 30°; and though some of these numbers are not in the exact order, and in other cases, as of olefiant gas and nitrous oxide, the curves sometimes even cross each other, these circumstances are easily accounted for by the facts already stated of irregular composition and the inevitable errors of first results. There seems every reason therefore to expect that the increasing elasticity is directly as the volatility of the substance, and that by further and more correct observation of the forces, a general law may be deduced, by the aid of which, and only a single observation of the force of any vapour in contact with its fluid, its elasticity at any other temperature may be obtained.

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* POGGENDORFF'S Annalen, xxiii. 290; or THOMSON on Heat and Electricity, p. 9.

Whether the same law may be expected to continue when the bodies approach near to the CAGNIARD DE LA TOUR state is doubtful. That state comes on sooner in reference to the pressure required, according as the liquid is lighter and more expansible by heat and its vapour heavier, hence indeed the great reason for its facile assumption by ether. But though with ether, alcohol and water, that substance which is most volatile takes up this state with the lowest pressure, it does not follow that it should always be so; and in fact we know that ether takes up this state at a pressure between thirty-seven and thirty-eight atmospheres, whereas muriatic acid, nitrous oxide, carbonic acid and olefiant gas, which are far more volatile, sustain a higher pressure than this without assuming that peculiar state, and whilst their vapours and liquids are still considerably different from each other. Now whether the curve which expresses the elastic force of the vapour of a given fluid for increasing temperatures continues undisturbed after that fluid has passed the CAGNIARD DE LA TOUR point or not is not known, and therefore it cannot well be anticipated whether the coming on of that state sooner or later with particular bodies will influence them in relation to the more general law referred to above.

The law already suggested gives great encouragement to the continuance of those efforts which are directed to the condensation of oxygen, hydrogen and nitrogen, by the attainment and application of lower temperatures than those yet applied. If to reduce carbonic acid from the pressure of two atmospheres to that of one, we require to abstract only about half the number of degrees that is necessary to produce the same effect with sulphurous acid, it is to be expected that a far less abstraction will suffice to produce the same effect with nitrogen or hydrogen, so that further diminution of temperature and improved apparatus for pressure, may very well be expected to give us these bodies in the liquid or solid state.

Royal Institution,
Feb. 19, 1845.

APPENDIX.

MR. NORTHMORE'S PAPERS ON THE COMPRESSION OF GASES.

(*Referred to at p.* 28.)

I.

Experiments on the remarkable Effects which take place in the Gases, by Change in their Habitudes, or elective Attractions, when mechanically compressed. By THOMAS NORTHMORE, *Esq. In a Letter from the Author.*[*]

To Mr. NICHOLSON.

Devonshire Street, Portland Place
SIR, *Dec.* 17, 1805.

IT was my intention to have postponed troubling you with the following experiments upon the condensation of the gases, until I had brought them to a greater degree of perfection; but being informed that several of them have already, by means of which I am ignorant, and probably in a mutilated state, found their way to the press, any further delay seems improper. If then you deem the present communication worthy a place in your interesting Journal, it is entirely at your service.

It had long ago occurred to me, that the various affinities which take place among the gases under the common pressure of the atmosphere, would undergo considerable alteration by the influence of condensation ; and the success attending the *violent* method adopted by the French chemists, which violence did not appear to me requisite, afforded additional encouragement to my undertaking some experiments upon the subject.

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[*] [From Nicholson's Journal, vol. 12 (1805), pp. 368-373.]

I communicated this to the late chemical operator in the Royal Institution, a gentleman eminently conversant in the science, and with whom I was then engaged in a series of experiments : he not only approved of my design, but seemed to think it not improbable that an extensive field might thus be opened to future discoveries. Whether these opinions are justly founded, is now left for you, Sir, and the public to judge.

In entering upon a field entirely new, obstacles were of course to be expected : nor without reason ; for though I had applied to one of the most eminent philosophical instrument-makers in London, Mr. Cuthbertson, yet I began to fear, even at the outset, that his skill would be set at defiance. The first instruments which he made for the present purpose were, a brass condensing-pump, with a lateral spring for the admission of the gas by means of stop-cock and bladder ; two pear-shaped receivers, one of metal of the capacity of seven cubic inches, and another of glass of about three and a half : these were connected by a brass stop-cock, having a screw at each end. The metallic receiver was soon found to be of little or no utility, as well on account of its liability to be acted upon by the generated acids ; its being too capacious, and thus consuming too large a quantity of gas : as because, though the result of an experiment might thus be known, yet the changes which the subjects might undergo would necessarily escape observation. The glass receiver obviated all these difficulties, and one or two imperfect experiments were performed with it : but the stop-cock speedily failed in its effect. For the power of the compressed gases was so great, partly from their elasticity, and partly (where affinities had operated) from their corrosive quality, as absolutely to wear a channel in the metal of which the plug was made, and thus to effect their escape. But not to trouble you any further with the obstacles that occurred, and which are mentioned only to prevent unnecessary expence to others, I have at last, by Mr. Cuthbertson's assistance, procured a connecting-tube, to which a spring-valve is adapted that has hitherto answered every purpose.

The instruments which I now use, are, 1st. An exhausting syringe; 2d. A condensing-pump, with two lateral springs for different gases; 3d. The connecting spring-valve; and lastly, glass receivers, which should have been of various sizes, but the one mentioned above having burst, that which I have principally used in the following experiments, is of about five cubic inches and a quarter in capacity, and made of glass well annealed and a quarter of an inch in thickness. Besides these instruments, I have occasionally applied Mr. Cuthbertson's double syphon-gage, by which the number of atmospheres condensed in the receiver, or rather the elastic power of the gases, may be measured; but this is rendered of less service, because a stop-cock must then be placed between the receiver and spring-valve, which frequently impairs the whole experiment; and also because, after a certain degree of condensation, and more particularly upon the admixture of the gases, new affinities usually take place, which tend to diminish the elasticity: the greatest number of atmospheres my gage has yet measured, is eighteen. These, Sir, with some bladders and stop-cocks, various iron screw-keys, and a wooden guard for the legs in case of bursting, constitute the principal part of the requisite apparatus.

I now proceed to the experiments, premising that the first four were made with the imperfect apparatus, when the gas was continually making its escape through the stop-cock.

Experiment I.

Into the glass receiver, of three cubic inches and a half capacity, were compressed in the following order: Hidrogen, two (wine) pints; oxigen, two pints; nitrogen, two pints. The result was, water which bedewed the inside of the receiver; white floating vapours (probably the gaseous oxide of nitrogen); and an acid which reddened litmus paper. Mr. Accum was present at this experiment, and from his opinion, as well as from succeeding experiments, I have reason to think that this acid is the nitric.

Experiment II.

As a difference of arrangement in the order of the gases tends considerably to vary the result, I repeated the former experiment (having first poured a little lime-water into the receiver) by injecting first the oxigen, about three pints, then equal quantities of hidrogen and nitrogen. Much of this gas escaped, owing to the imperfection of the instrument; but upon the affusion of the nitrogen, the white vapours again appeared in the receiver; water seemed likewise to be formed; and some yellow particles were seen floating upon the lime-water. These particles probably arose from the resinous sub stance, used in fastening on the cap of the receiver, being dissolved by the nitrous gas formed during condensation.

I would just observe, that the magnet *seemed* to be affected during this experiment; but as there is iron used in the machine, this may be otherwise accounted for.

Experiment III.

Two pints of carbonic acid, and two of hidrogen, were subjected to condensation. The result was, a watery vapour, and a gas of rather offensive smell.

Experiment IV.

Trying to inflame phosphorus by the condensation of atmospheric air, the bottom of the machine (where it had been repaired) burst out with an explosion. This happened when I had immersed the apparatus in water to discover where the air escaped. The receiver was full of the fumes of the phosphorus, which was itself dispersed in the vessel of water. I afterwards repeated this experiment with the more perfect apparatus, but I could not inflame the phosphorus, and the fumes which arose at first soon disappeared. There was just enough acid (probably phosphoric) formed in the inside of the receiver to tinge litmus.

Experiment V.

Having now the spring-valve, and new receiver of five cubic inches and a half capacity, I poured in two scruples of solution of potash, and then injected two pints of hidrogen, two of nitrogen, and three of oxigen. This quantity was hardly sufficient for the capacity of the receiver, and the result was only a smell of the gaseous oxide of nitrogen, a few yellowish fumes, and scarce enough acidity to tinge the edge of the test paper: of course, I could not effect the formation of nitrate of potash.

Experiment VI.

I now determined to begin with the nitrogen, which always appeared to me to undergo the most important chemical changes, and therefore injected two pints of nitrogen, three of oxigen, and two of hidrogen. Upon the condensation of the nitrogen, it speedily assumed an orange-red colour, which upon the accession of the oxigen, gradually diminished, and at length disappeared, though at first it seemed rather deeper. A moist vapour, coating the inside of the receiver, arose upon the compression of the hydrogen, which moisture was strongly acid to the taste, coloured litmus, and, when very much diluted with water, acted upon silver.

Experiment VII.

Nearly the same as the last, but with different arrangement. The nitrogen, three pints and a half, was first introduced; then the hidrogen,* two pints; and next the oxigen, three and a half. The nitrogen formed the orange-red colour as before; the hidrogen produced white clouds at first (*quære* ammonia?) which afterwards disappeared, and the orange-red colour became lighter; but upon the affusion of the oxigen, the colour did not disappear as in the last experiment, but, if any thing, became darker. I then injected two pints more of hidrogen, but this had little or no effect upon the colour. Some vapour was generated, which was, as usual, strongly acid.

Experiment VIII.

Previous to the bursting of the small receiver, I had put in it a scruple of lime, and condensed upon it three pints of nitrogen. The result was, a little reddish colour at first, which soon vanished. Upon repeating this experiment in the large receiver, I could produce no colour at all. In my present state of knowledge I am unable to account for this circumstance; but as soon as I get my new receivers of a smaller capacity, I mean to repeat the experiment.

Besides the above, I have made various other experiments with different gases, but I think it right to repeat them with greater accuracy before I submit them to the eye of the public: if upon that repetition they appear to me to be attended with results of sufficient importance to occupy a place in your Journal, I will take the liberty of communicating them to you, and am, Sir,

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* [Oxigen in the original.]

Your most obedient servant,
THO. NORTHMORE.

P. S. I think it necessary to add, that during the course of the above-mentioned experiments, there was a great variation of temperature in the atmosphere, from the heat of 70 degrees of Fahrenheit to the cold of 33.

II.

Experiments on condensed Gases. By T. NORTHMORE.*

To Mr. NICHOLSON.

SIR,

I NOW take the liberty of presenting you with a continuation of my experiments upon the condensation of the gases, but first beg leave to make one observation, viz. that the quantity of gas said to be injected in each experiment, cannot (particularly in the preceding article) always be depended upon; for its tendency to escape is so constant and powerful, as frequently to elude every effort of mine to prevent it, and if it can find no other exit, it will sometimes escape by the side of the piston of the forcing pump. In the preceding experiments I have endeavoured as much as possible to obviate this evil, but not always with the success that I could wish.

Repeating the eighth experiment mentioned in my former letter, (see Vol. XII. p. 372-3) viz. the condensation of nitrogen upon lime, in order to discover the cause of the loss of colour in the nitrogen, I perceived that this arose from its fixation, and a nitrate of lime was the result. This experiment, on account of the elasticity of nitrogen previous to its change of habitude, requires some caution ; for one of my best receivers, three-eighths of an inch thick, was shivered in pieces with a violent explosion, after I had set it aside to see the effect of time upon the compressed gas.

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* [From Nicholson's Journal, vol. 13 (1806), pp. 233-236.]

Experiment 9. Upwards of a pint of nitrogen was condensed, and upon this I pumped one pint of gaseous oxide of carbon. The colour of the nitrogen was destroyed ; nitrous acid was formed ; and upon collecting the liberated gaseous oxide, it burnt not unlike alcohol. The two gases together were at first highly elastic.

From the facility with which nitrogen becomes united and fixed in various bodies, and from its expansive force when liberated from that state, I know not whether I am sufficiently warranted in suggesting an opinion, that the explosive force of various compounds may in a great measure be attributed to the sudden liberation of this fixed gas. To this cause I partly attribute the fulminating silver of Berthollet ; the fulminating gold, and various nitrates ; and the detonation which accompanies the decomposition of ammoniac by oxigenated muriatic acid gas.

Exp. 10. Having been unsuccessful in my endeavours to inflame phosphorus by the compression of atmospheric air, (see *Exp.* 4.) I now tried oxigen, but with little better effect. The phosphorus appeared to be somewhat discoloured, and I thought had a tendency to liquify, as it does when put upon a heated plate of iron. Indeed I have no doubt that some heat is generated by the condensation of air, since the thermometer rises upon external application to the receiver.

Exp. 11. Upon the compression of nearly two pints of oxigenated muriatic acid gas in a receiver two and a quarter cubic inches capacity, it speedily became converted into a yellow *fluid*, of such extreme volatility under the common pressure of the atmosphere, that it instantly evaporates upon opening the screw of the receiver. I need not add, that this fluid, so highly concentrated, is of a most insupportable pungency. When atmospheric air was pumped into the empty receiver, it was speedily filled with dense white fumes. There was a trifling residue of a yellowish substance left after the evaporation, which probably arose from a small portion of the oil and grease used in the machine, mixed with some of the concentrated gas; it yielded to sulphuric ether, and destroyed vegetable colours.

This gas is very injurious to the machine, and on that account difficult to work.

Exp. 12. Upon half a pint of oxigen was injected one pint of oxigenated muriatic acid gas. The result was a thicker substance, which did not so soon evaporate, and a yellowish mass was left behind.

Exp. 13. Upon half a pint of nitrogen was injected one pint of oxy-muriatic gas. The result was a still thicker substance, and the yellow colour deeper, nor did it appear to act so powerfully upon vegetable colours. Much of the grease of the machine was carried down in both these last experiments, which formed part of the yellow residue, and yielded only to ether.

Exp. 14. Having condensed about a pint of carbonic acid, the receiver very unexpectedly burst with violence. This circumstance I attribute to the vicinity of the furnace, and I mention it to guard others against standing too near a fire in these experiments; nor perhaps may it be useless to add another precaution, that of using goggles, or at least a thick plate of glass when examining the results.

I now took a new receiver of three cubic inches of capacity, and pumped in one pint of carbonic acid, and upon this rather more than a pint of oxigenated muriatic acid gas.

The union produced a light sap-green colour, but no fluid, though as usual the oil of the machine had retained enough efficacy to destroy vegetable colours.

Exp. 15. Upon rather more than a pint of hidrogen, which was highly elastic, were compressed two pints of the oxigenated muriatic gas. The result was a light yellow-green colour, and no fluid. Some smoke or vapour seemed to issue out of the receiver upon turning the screw, and the gas was highly destructive of colouring matter.

Exp. 16. I now proceeded to the muriatic acid gas, and upon the condensation of a small quantity of it, a beautiful green coloured substance adhered to the side of the receiver, which had all the qualities of muriatic acid; but upon a large quantity, four pints, being condensed, the result was a yellowish-green glutinous substance, which does not evaporate, but is instantly absorbed by a few drops of water; it is of a highly pungent quality, being the essence of muriatic acid. As this gas easily becomes fluid, there is little or no elasticity, so that any quantity may be condensed without danger. My method of collecting this, and other gases which are absorbable by water, is by means of an exhausted florence flask (and in some cases an empty bladder) connected by a stop-cock with the extremity of the retort.

An idea here occurs to me, that the facility of fixation which is the property of the compressed muriatic, oxy-muriatic, and some other gases, may be made of some utility to the arts, since by previously pouring in a little water, or other fluid into the receiver, an acid may be obtained of almost any degree of concentration.

Exp. 17. Having collected about a pint and a half of sulphureous acid gas, I proceeded to condense it in the three cubic inch receiver, but after a very few pumps the forcing piston became immoveable, being completely choked by the operation of the gas. A sufficient quantity however had been compressed to form vapour, and a thick slimy fluid of a dark yellow colour began to trickle down the sides of the receiver, which immediately evaporated with the most suffocating odour upon the removal of the pressure. This experiment corroborates the affirmation of Monge and Clouet, mentioned in Accum's chemistry, vol. I. p. 319. viz, that "by extreme artificial cold, and a strong pressure exerted at the same time, they rendered sulphureous acid gas fluid. From the injury which this gas does to the machine, it will be very difficult to perform any experiments upon its elective attractions with the other gases.

I remain, Sir,
Your obedient humble Servant,
T. NORTHMORE.

Devonshire Street, Portland Place,
Feb. 15, 1806.

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Alembic Club Reprints—No. 13.

THE EARLY HISTORY

OF

CHLORINE.

Papers by
CARL WILHELM SCHEELE
(1774).

C. L. BERTHOLLET
(1785).

GUYTON DE MORVEAU
(1787).

J. L. GAY-LUSSAC and L. J. THENARD.
(1809).

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PREFACE.

THE history of chlorine forms one of the most interesting and important chapters in the whole of chemistry, and this collection of papers is issued in order that students may have access to all the important early work on the subject. The volume containing Davy's researches (Reprint No. 9) may be taken as a continuation of the present one.

The first paper contains Scheele's description of the discovery of chlorine, made accidentally when he was investigating the properties of "Brunsten" (black oxide of manganese). It is interesting to note, not only his clear and wonderfully correct views as to the nature of the substance, but also the very full description of it which he gives in a small space.

In marked contrast to the preceding one is the long paper by Berthollet, in which, carried away by his zeal for Lavoisier's doctrines, he propounds the view that chlorine is the higher oxide of an as yet unknown radical. This view, although founded so loosely, obtained general adoption, and became so firmly rooted that it was only given up after one of the fiercest controversies connected with the science.

The extract from de Morveau's Memoir is reprinted simply to shew clearly the position of chemists at that time. Although not directly connected with the matter in hand, it is perhaps permissible to call the attention of any chemists who use the expression "radicle" to the historical authority for "radical" contained in the second paragraph of the extract.

The extracts from Gay-Lussac and Thenard bring us to the time of Davy. These three investigators were simultaneously engaged in investigating the properties of chlorine and hydrochloric acid, and endeavouring to isolate the radical. Before long, Davy concluded that chlorine contained no oxygen, but was itself an element; this view was not adopted by his rivals till considerably later. Nevertheless, it is sometimes claimed that Gay-Lussac and Thenard first established the elementary nature of chlorine. This claim is apparently founded on the statement at the end of the paper now reprinted (p. 48). That it is not justified is clearly shewn by the extract from their "Physico-chemical Researches" given at the end of the present volume.

As in the other translations of the Alembic Club Reprints, the endeavour has been to give a fairly accurate reproduction of the author's language rather than an elegant version.

H. M.

ON MANGANESE

And its Properties.

BY CARL WILHELM SCHEELE.*

* * * * *

Behaviour of Manganese with common Marine Acid.

6. (*a*) One ounce of pure *spiritus salis* was poured on half an ounce of finely-ground manganese. After this mixture had stood one hour in the cold, the acid had assumed a dark brown colour. Part of this solution was poured into a bottle, which was left open in a warm place. The solution gave off a smell like warm *aqua regis*, and after a quarter of an hour it was clear and colourless as water, and the smell was gone. (*b*) The remainder of the brown mixture was set to digest, in order to see whether the marine acid would saturate itself with manganese. As soon as the mixture became warm, its smell of *aqua regis* became considerably augmented, and an effervescence also arose, which continued till the following day, when the acid was found to be saturated. On the residue which it had been unable to dissolve, there was again poured one ounce of *spiritus salis*, whereupon all the above-mentioned phenomena occurred, and the manganese became completely dissolved, except a little siliceous earth.

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23. The sixth paragraph shews the behaviour of manganese with marine acid. In this case it is not so easy

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* [Translated from "Om Brunsten, eller Magnesia, och dess Egenskaper," Kong. Vetenskaps Academiens Handlingar, xxxv., pp. 89, 93, 94, 105-110. Stockholm, 1774.]

to understand at first whence the manganese has obtained its phlogiston; nothing combustible is added here, and nevertheless the complete dissolution of the manganese can be effected without heat. In fact, there occurs here a phenomenon which proves that phlogiston is certainly present in marine acid—a property which one would have attributed to nitrous acid, since chemists, subsequent to STAHL, have believed that this principle is required in considerable quantity as one of its constituents. That, however, we may now reverse and attribute to marine acid.

When marine acid stood over manganese in the cold it acquired a dark reddish brown colour (§ 6, *a*). As manganese does not give any colourless solution without uniting with phlogiston, it follows that marine acid can dissolve it without this principle. But such a solution has a blue or a red colour (§ 14, No. 4). The colour is here more brown than red, the reason being that the very finest portions of the manganese, which do not sink so easily, swim in the red solution; for without these fine particles the solution is red, and red mixed with black makes brown. The manganese has here attached itself so loosely to *acidum salis* that water can precipitate it, and this precipitate behaves like ordinary manganese. When, now, the mixture of manganese and *spiritus salis* was set to digest, there arose an effervescence and smell of *aqua regis* (§ 6, *b*).

In order clearly to apprehend this novelty I took a retort containing a mixture of manganese and *acidum salis*. In front of the neck I bound a bladder emptied of air,* and set the retort in hot sand. The bladder became distended by the effervescence in the retort. When the acid no longer effervesced, which was an indication of its saturation, I removed the bladder, and

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[* Compare Alembic Club Reprint, No. 8, § 30.]

found that this air had coloured it yellow, as if by *aqua fortis*, but did not contain any trace of *aer fixus;* it had, however, a quite characteristically suffocating smell, which was most oppressive to the lungs. It resembled the smell of warm *aqua regis.* The solution in the retort was clear, inclining to yellow, which last mentioned colour was caused by its containing iron. If one wishes to be convinced that this dissolved manganese contains phlogiston, let him precipitate the solution with *alkali tartari*, edulcorate the precipitate, and then proceed therewith as is described in § 15, *a*, *b*, *c*. But whence has this manganese obtained phlogiston? From *acidum salis.* Here we cannot have recourse to heat, because the solution becomes clear without it, only it must stand several hours in the open air. What happens to the solution is as follows: The manganese is first attracted by the marine acid, whence a brown solution arises. By the help of the acid this dissolved manganese acquires a strong attraction for phlogiston (§ 14, No. 2), and actually draws it to itself from the particles of acid with which it is united. This part of the acid, which has thus lost one of its constituents and is only very loosely united to the now more phlogisticated manganese, is driven out from its earth by the remaining marine acid which has not yet suffered any decomposition, and appears then, with effervescence, as a highly elastic air, or similar fluid; the brown colour has then disappeared and a water-clear solution resulted.

24. This marine acid, deprived of phlogiston as one of its constituents, unites with water in very small quantity; and gives the water a slightly acid taste; but as soon as it comes in contact with a combustible matter it becomes again a proper marine acid. In order to investigate the properties of this air it is best to put it to the test in the elastic state. Ordinary marine acid

is mixed with finely-ground manganese, in any chosen quantity, in a glass retort which is placed on warm sand; small bottles which hold about twelve ounces of water are employed as receivers; about two drachms of water are put into each bottle, and the joints are not luted except by means of grey paper wrapped round the neck of the retort, and on this the bottle is fixed. When a bottle has remained a quarter of an hour or more, it is found, according to the quantity of the elastic acid in the receiver, that the air in it assumes a yellow colour; the bottle is then removed from the retort.

If the paper luting has held tight, a part of the air escapes with force; a previously fitted cork is then immediately inserted into the bottle, and another bottle is fixed to the neck of the retort in its stead. In this way several bottles can be partly filled with dephlogisticated marine acid. It is to be noted that the retort must be placed in such a position that in case drops should rise into the neck they can flow back. The water in the bottles serves this purpose, that, should any vapour of muriatic acid pass over, it may have this water to which it may betake itself. I take more than one bottle so that it is not necessary for me to start a new distillation for each experiment that I make. It is not advantageous to fill large globes, as a good deal of the acid escapes into the air every time they are opened.

25. Whatever was experimented with in this dephlogisticated marine acid was hung on a glass tube which I fastened into the cork. (*a*) The corks in the bottles became yellow, as from *aqua fortis*, and during the distillation the luting was likewise attacked. (*b*) Blue litmus paper became almost white; all vegetable flowers—red, blue, and yellow—became white in a short time; the same thing also occurred with green plants. In the meantime the water in the bottle became changed to a

weak and pure marine acid. (*c*) The former colours of these flowers, as well as those of the green plants, could not be restored either by alkalies or by acids. (*d*) Expressed oils and animal fats, when they hung as drops on the glass tube or were rubbed on it, became in a short time tough like turpentine. (*e*) Cinnabar became white on the surface, and when the piece was washed in water a pure *mercurius sublimatus* solution was obtained, but the sulphur was not altered. (*f*) Iron vitriol became red, and deliquesced. Copper and zinc vitriols were unaltered. (*g*) Iron filings were put into the same bottle and they dissolved. This solution was evaporated *ad siccum* and distilled with addition of oil of vitriol, when a pure marine acid, which did not dissolve gold, again passed over. (*h*) All metals were attacked, and with gold it is noteworthy that its solution in this dephlogisticated marine acid forms with *alkali volatile* an *aurum fulminans.* (*i*) When *spiritus salis ammoniaci*, prepared with lime, hung in drops on the tube, there arose a white cloud, and a quantity of air bubbles escaped from the drops, which gave off a smoke when they burst asunder. (*k*) *Alkali fixum* was changed into *sal commune* which decrepitated on charcoal, but did not detonate. (*l*) Arsenic deliquesced in these vapours: (*m*) Insects immediately died in them; (*n*) and fire was immediately extinguished by them.

26. This proves sufficiently the great attraction which dephlogisticated marine acid has for the combustible.* It is possible that STAHL obtained such a dephlogisticated marine acid by means of iron, as he concludes from the yellow colour on the cork, and imagined that the marine acid was changed into nitrous acid. If a mixture of

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* ["Den brenbara" might be translated "phlogiston;" but Scheele also uses the latter word, so the literal translation is adopted here.]

manganese, *spiritus salis*, or *spiritus vitrioli*, and *alcohol vini* is digested several days in a well-closed flask, and thereafter gently distilled, there arises no effervescence, but *spiritus vini* passes over; it has, however, and this is noteworthy, a strong smell of *aether nitri*. The residue in the retort has lost its acid, and is saturated with manganese. If metals, sugar, turpentine, or linseed oil are added to a mixture of ground manganese and marine acid there arises no dephlogisticated marine acid; for here there is sufficient combustible present with which this elastic acid can combine. With mercury it is noteworthy that a good deal of it also goes into the solution, from which it can be obtained by crystallisation, and behaves like corrosive sublimate. If leaves of pure gold are put into a mixture of ground manganese and pure *acidum salis*, it is found afterwards that this solution contains gold, as well as manganese, dissolved.

MEMOIR

On Dephlogisticated Marine Acid.

By M. Berthollet.*

The important experiments by which the nature of water had just been determined, and the happy application which M. de la Place had made of them to the production of inflammable gas by the dissolution of metals, threw great light on the whole of chemistry; phlogiston, that principle which Stahl had ingeniously imagined in order to account for a large number of phenomena, and by means of which there was really established between them a connection which has served for a long time to guide chemists in their researches, appeared to me to have at last become a useless hypothesis, whereupon I believed it incumbent on me to subject dephlogisticated marine acid to new experiments, as its properties might destroy or confirm the opinion I had adopted. These experiments were the subject of a memoir which I read at the public meeting of 6th April 1785. I shall now enter into greater detail, add some new observations, and reply to some objections which have since then been made to the theory which I had established.

Scheele, when investigating the effects which different acids produced on manganese, observed that muriatic acid produced an effervescence with it, and that there was disengaged a vapour similar to that from hot aqua regia. He says, "The manganese is first attracted by the muriatic acid, thereafter it acquires, by means of the acid, a stronger affinity for phlogiston, and then it abstracts the latter from the particles of the acid with which it has not itself combined. This portion, thus deprived of one of its constituent parts and feebly united to the phlogisticated manganese, is sublimed by the rest of the acid which is still undecomposed, and manifests itself, with effervescence, as a very elastic air or as a fluid resembling air.

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* [Translated from "Memoires de l'Académie Royale" for the year 1785. Pp. 276-295. Paris, 1788.]

Muriatic acid deprived of phlogiston, which is one of its constituent parts, only unites with water in very small quantity and does not render it strongly acid, but as soon as it meets with a phlogisticated substance it becomes again a true muriatic acid. It is in its elastic state that the qualities of this air are best shewn."

He thereafter describes how this vapour ought to be collected in small flasks which are adapted to the neck of the retort, and in which a little water has been placed.

Bergman adopted Scheele's view; with him he regards manganese as a substance very avid of phlogiston, and believes that it removes this principle from the marine acid, which thereby acquires the properties characterising the gas of dephlogisticated marine acid, and that this gas acts upon substances which contain phlogiston by removing this principle from them. It is to these two illustrious chemists that we owed the chief and almost the only ideas which we had about dephlogisticated marine acid when I turned my attention to it.

I commenced by assuring myself that dephlogisticated marine acid, in the form of gas, combined with water more easily and more abundantly than acid of chalk. After that, I tried to saturate water with it in the least embarrassing manner and without exposing myself to breathing it, for it is suffocating. SCHEELE in his experiments employed one part of manganese to two of marine acid; but I have found that one part of manganese to four parts of fuming marine acid, or to six of ordinary marine acid, is sufficient, and even that in these proportions there is a fairly considerable portion of manganese which is not attacked by the marine acid. I pour the marine acid on the pulverised manganese contained in a tubulated retort to which I have previously adapted an empty bottle, and, successively, in the manner of M. WOULF, three other bottles almost filled with water; the last bottle communicates by a tube with a vessel which is filled with water, and on which, when the air of the apparatus is expelled and the smell of dephlogisticated marine acid begins to be perceptible, I invert a large bottle likewise full of water.

If I employ fuming marine acid the gas begins to come off in abundance without the necessity of applying heat to the retort, but if the marine acid is of only medium strength I put a slight fire below the retort from the commencement, and augment it gradually until the liquid enters into ebullition; shortly after the ebullition has commenced, the operation comes to an end; its termination is announced by the drops of marine acid which fall from the beak of the retort into the first bottle.

As absorption proceeds, the water assumes a greenish yellow colour, and when it approaches saturation the gas assumes a concrete form; in this state it gradually descends to the bottom of the liquid in small yellowish flakes, so that its specific gravity is a little greater than that of the saturated water; but, to obtain it in this form, it is necessary that the temperature of the place where the experiment is performed should not be too far from the freezing point, and further, the bottles should be surrounded by pounded ice, or, if they are relatively too large, it may even be necessary to saturate the liquid by a second operation. Each ounce of marine acid employed suffices to saturate about a pint of water. In a second operation the water contained in the inverted bottle, which has absorbed that portion of the gas which could not enter into combination in the bottles of the apparatus, may be employed for filling these; by this means there is no loss of the gas, and breathing it is avoided.

The concrete form of dephlogisticated marine acid resumes the gaseous state when it is exposed to a feeble degree of heat; if the hand is placed upon the bottom of the bottle which contains it, it is seen to resolve itself into bubbles which rise to the surface; hence it is difficult to preserve it in closed vessels; a part, however, dissolves again in the liquid. It is chiefly in the liquid state that I have examined dephlogisticated marine acid; to determine its specific gravity I decanted the liquid from the concrete part, the thermometer being at 5 degrees above zero, and I found it to be 1003. It has a harsh taste which does not resemble that of the acids. SCHEELE and BERGMAN have observed that it destroyed vegetable colours; and it produced this effect, which I shall analyse further on, more or less promptly without any red tint becoming perceptible. A property which specially merits attention is that it does not cause an effervescence with solution of fixed alkali even when the latter is saturated with fixed air. The fixed alkalies, nevertheless, contract an affinity, and combine with it; for they cause it to lose its colour and a great part of its odour, as lime also does. If, after having added the alkali, acetous acid is poured into it, an effervescence is seen to be immediately produced, as if the alkali were simply dissolved in the water, and the odour regains all its sharpness.

The calcareous earth, when it is in the effervescent state, has also the property of combining with dephlogisticated marine acid, and dissolves in it in fairly considerable quantity; it is precipitated from it by all the alkalies, and even by lime water; which proves that lime combines with this liquid more strongly than effervescent calcareous earth does.

We can therefore, as it seems to me, regard dephlogisticated marine acid as almost entirely deprived of acidity. SCHEELE and BERGMAN were unable to recognise this essential property, as in the process which they employed the water of the vessels in which they received the gas could contain only a very small portion of dephlogisticated marine acid, mixed with a portion of marine acid which always passes over in the distillation; in my apparatus this portion of marine acid is retained in the first bottle, which I leave empty, and which it is well to surround with ice or cold water. When the operation is not made with sufficient care a little marine acid passes even into the first bottle which is filled with water; this accident can be easily recognised by pouring into the liquid some solution of effervescing fixed alkali; if any bubbles are seen to be disengaged this is a proof that it contains some marine acid, for it should not produce any effervescence.

In a retort at the pneumato-chemical apparatus, I boiled a mixture of mineral alkali and dephlogisticated marine acid; much gas was disengaged, of which a great part was fixed air, and the other part at first atmospheric air and then air purer than this, but the last portions were hardly anything but fixed air. With lime there is no fixed air disengaged, but atmospheric air which gradually approaches to vital air, and finally a little very pure vital air. The fixed air of the first experiment is thus furnished by the alkali, as it is in the effervescences, the atmospheric air is due to the space which I left empty in the apparatus, and the vital air to the dephlogisticated marine acid.

The salt which is found in the retort is similar to sea salt, which explains the observation of SCHEELE and BERGMAN as to the identity of the neutral salts formed by dephlogisticated marine acid with those of ordinary marine acid. They were obliged to suppose that the alkalies imparted some phlogiston to the dephlogisticated marine acid and that too without themselves suffering any alteration in their properties by this loss.

I calcined some manganese at a strong heat in a pneumato-chemical apparatus. I extracted from it, as had already been observed, a large quantity of vital air; it lost an eighth of its weight. In this state I treated it with marine acid and obtained from it a much smaller quantity of dephlogisticated marine acid.

It is therefore to the vital air of the manganese, which combines with the marine acid, that the formation of the dephlogisticated marine acid is due. I ought to state that this theory was presented and announced some time ago by M. LAVOISIER, and that M. DE FOURCROY has made use of it in his Elements of Chemistry and Natural History to explain the properties of dephlogisticated marine acid such as they were then known.

The experiments which I have just described have not appeared sufficiently conclusive to some chemists; I shall take from the first part of the learned Dictionary of Chemistry, which M. DE MORVEAU has just published, the reasons which can be adduced to prove the necessity of phlogiston in the explanation of the properties of dephlogisticated marine acid. I reduce to three the objections of this celebrated chemist: 1.° marine acid does not combine with vital air in the elastic state, how could it remove it from a substance by a simple affinity? 2.° when dephlogisticated marine acid combines with the alkalies, the earths, or the metals, there is nothing to prove that it does not receive phlogiston or inflammable gas from them in exchange; *for this fluid*, according to M. DE MORVEAU, *is nothing but phlogiston itself brought into the state of gas by the matter of heat;* 3.° the differences which manganese presents in the states of regulus, of white calx, and of black calx, and the effects which it produces when it is treated before the blow-pipe or when it is mixed with other substances can only be explained by means of phlogiston.

But, 1.° the elastic state of a fluid is an obstacle to combination, whatever may be the cause which holds the parts of the fluid in expansion; this is a general fact, for the explanation of which phlogiston is of no service, for, at a low temperature, vital air cannot combine with inflammable gas in the elastic state, although, according to M. DE MORVEAU, inflammable gas is nothing but phlogiston, and vital air has a great affinity for it. If, then, we do not go back to the cause of the elasticity of fluids, the difficulty is no less great in following the opinion of M. DE MORVEAU; but if we regard vital air as a compound of the principle of light or of heat with a base, as experiments prove, there remains much less obscurity for those who reject the theory of phlogiston. In fact, a substance must be in a state to overcome the affinity which the principle of light has for the base of vital air, in order to expel the former, and form with the latter a new compound; but marine acid has a very feeble affinity for vital air, it cannot combine with it except by compound affinities, and easily gives it up to all substances with which this principle has any affinity. There will be found at the end of this memoir explanations regarding the third objection.

2.° I saturated distilled water with dephlogisticated marine acid, but although I repeated the operation three times, and the bottle was well surrounded with ice, I could not obtain any in the concrete form, because the thermometer was at 18 degrees. With this liquid I filled a bottle communicating by means of a tube with a pneumato-chemical apparatus; this bottle with the tube, which was itself filled with the liquid, was of the capacity of 51.1 cubic inches; I exposed it to sunlight; I soon saw a large quantity of small bubbles become disengaged, which, on being collected in a bottle filled with water, formed at the end of several days a volume of air of 15.27 cubic inches, the thermometer being at 17 degrees. The dephlogisticated marine acid lost its colour gradually; in this state the liquid no longer destroys blue vegetable colours but reddens them strongly, like ordinary marine acid; it produces an effervescence with fixed alkalies; it retains an odour of dephlogisticated marine acid which is scarcely perceptible; in fine, it is reduced almost entirely to ordinary marine acid.

To determine the quantity of this acid which was present in the liquid, I precipitated it by a solution of silver, and, with the same solution, I also precipitated 500 grains of marine acid, of which the specific gravity was to that of distilled water as 1141 is to 1000, and which I had diluted with distilled water. The two precipitates were dried equally; the 500 grains of marine acid gave 7 gros 43 grains of muriate of silver, and the dephlogisticated marine acid gave 5 gros 23 grains, so that, neglecting the volume of liquid which was put into the tube, 50.45 cubic inches of dephlogisticated marine acid contained 350.09 grains of marine acid of a specific gravity equal to that of the 500 grains employed, which comes to about 7 grains per cubic inch of liquid.

The air which was disengaged from the dephlogisticated marine acid having been put over a solution of liver of sulphur, was absorbed, leaving a residue of one cubic inch, so that it consisted of vital air, which contained one-fifteenth of mephitic air, the latter being without doubt due to some atmospheric air which would be disengaged both from the water and from the apparatus which I employed. I do not deduct its volume, however, because there remained a small portion of dephlogisticated marine acid which had resisted decomposition, and because the water was impregnated with vital air, so much so, that on agitating it, bubbles escaped from it; there would rather be a small addition to make.

Accordingly 51.1 cubic inches of liquid contained 15.27 cubic inches of vital air, at the temperature of 17 degrees, which makes about 0.299 cubic inch of vital air per cubic inch of liquid; but I need not state that in these calculations I do not profess to give anything but approximations.

In an experiment made with dephlogisticated marine acid which had been obtained at a lower temperature, and which had been decanted from a concrete portion, I found that the liquid contained about a quarter less of acid and of vital air; so that dephlogisticated marine acid follows in its combination with water, a law different from that followed by the other elastic fluids which can combine with it, which unite with it in greater quantity the more the temperature approaches the freezing point: this arises from the tendency of dephlogisticated marine acid gas to take the concrete form by means of cold; but this difference is limited within a very small compass, for as soon as the thermometer is some degrees above freezing point, dephlogisticated marine acid tends to separate from the water and resume the elastic state. Hence it appears that the best way to obtain this liquid very concentrated is to produce in it a fairly considerable quantity of concrete substance, and then to let this dissolve at a temperature approaching the 10th degree of Reaumur's thermometer; it is also at about this degree of heat that we can obtain the greatest effects of the liquid on the substances which are submitted to its action; and on applying heat this effect is diminished by the tendency towards the gaseous state which is communicated to the dephlogisticated marine acid. This consideration may also apply to various other chemical solutions, and serves to explain the interesting observation of M. de Butini, who noticed that aerated water dissolved so much the more magnesia the colder it was.

These experiments ought to dispel any doubts which might remain as to the nature of dephlogisticated marine acid; the latter is manifestly formed by the combination of vital air with marine acid, but in it the vital air is deprived of a part of the principle of elasticity, and adheres so feebly to the marine acid that the action of light suffices to disengage it promptly, light having more affinity for its base than marine acid has. There are, then, two conditions which dispose it to quit the marine acid in order to combine with substances with which it has affinity, and which render dephlogisticated marine acid proper to discover what are the properties which depend on combination with vital air, which could not have taken place except by more complicated or much slower means. It is vital air, then, which disguises the properties of dephlogisticated marine acid; it loses them as soon as that principle separates from it.

Dephlogisticated marine acid dissolves iron and zinc without any gas being disengaged, and in the same manner as water dissolves salt; for that these metals should dissolve in an acid it is only necessary that they should unite with a portion of vital air, as M. Lavoisier has proved; and as dephlogisticated marine acid can furnish them with the portion of vital air necessary when it dissolves them, there is no decomposition of water and no inflammable air is produced.

But, if one is inclined to suppose that light gives phlogiston to the dephlogisticated marine acid which is exposed to it, let us see what are the consequences which would follow therefrom. Firstly, it would require that the light should give phlogiston to dephlogisticated marine acid without communicating any to vital air, with which, however, it is believed that it has a very great affinity; secondly, as phlogiston is no other than inflammable gas, according to Messrs KIRWAN, DE MORVEAU, DE LA METHERIE, and some other chemists, it must be supposed that light contains a large quantity of inflammable gas and that the sun every instant suffers an immense loss of matter. Will one say that iron and zinc contain inflammable gas which they give to dephlogisticated marine acid whilst they combine with its vital air? The difficulty remains unaltered, for light would have to be able to decompose dephlogisticated marine acid just the same. If now, physicists cannot admit that light gives inflammable gas, I say that it would be proved by the experiment of which I have just spoken that iron and zinc do not contain inflammable gas, even although the direct experiments which have been made on this subject should not be decisive. Finally, chemists agree that the metals are reduced to calces when they are dissolved by means of marine acid, and consequently that they are combined with vital air; but it is not the marine acid which has been able to communicate the vital air to them, for it is not decomposed in these dissolutions; it must necessarily be the water then which furnishes it to them, as it must be it which gives the inflammable gas, as M. DE LA PLACE has shewn: these truths lend a mutual support.

When solution of mercurial nitre is poured into dephlogisticated marine acid no white precipitate is produced; but on evaporating the liquid, corrosive sublimate is obtained from it. Similarly, if white precipitate is put into dephlogisticated marine acid it dissolves, the odour and the colour of the dephlogisticated marine acid disappear, vegetable colours are no longer destroyed, and the marine acid is meanwhile in combination; for, on adding to the liquid a little lime water, there is immediately formed a mercurial precipitate, which would not take place if a portion of marine acid were free. Hence it results that the difference between white precipitate and corrosive sublimate consists in this, that in the latter the mercury is combined with a greater quantity of vital air and marine acid.

The manner in which dephlogisticated marine acid acts on mercury merits attention; if some of this liquid is put on a certain quantity of mercury, the surface of the metal blackens, there is formed the calx of mercury known by the name of *ethiops per se*, and the liquid reddens blue paper, so that the metal begins by removing the vital air from the marine acid. If they are still left in contact the calx of mercury which has been formed takes up marine acid and becomes white, it passes into the state of combination known by the name of *panacea*, and the supernatant water does not contain either acid or mercurial salt; if it be poured off and dephlogisticated marine acid anew added, there is at once formed a combination with the mercurial salt, which, according to the quantities of marine acid which it absorbs, takes successively the properties of *mercurius dulcis* and of white precipitate, and then, if the liquid is renewed, it dissolves and forms corrosive sublimate; so that in this experiment the whole series of mercurial muriates is obtained, to which corresponds that of their causticity.

Scheele announced that dephlogisticated marine acid had no action on sulphur, but M. de Morveau has ascertained that it changes it into vitriolic acid. When some is poured on a small portion of solution of hepar made with fixed alkali, there is no hepatic gas disengaged and there is only very little precipitate formed; the odour of the dephlogisticated marine acid is dispelled, and vegetable colours are no longer destroyed; but though hepar acts on them like the alkalies, the mixture of which I have just spoken indicates only an acid, and the solution of heavy spar occasions an abundant precipitate. These phenomena shew that a part of the sulphur of the hepar is changed immediately into vitriolic acid by the dephlogisticated marine acid.

I added water saturated with hepatic gas to dephlogisticated marine acid; the colour and the odour of the latter were destroyed, no precipitate was formed, vegetable colours were not altered except as they are by an acid, a solution of lead was precipitated white, and the solution of heavy earth formed an abundant precipitate; but if a little dephlogisticated marine acid is added to hepaticised water it becomes clouded and a little sulphur precipitates. In the first case the dephlogisticated marine acid and the hepatic gas are destroyed on the instant and entirely, if they are employed in the correct proportions; the sulphur and the inflammable gas which holds it in solution are reduced by combination with the vital air, the first to vitriolic acid and the second to water: but in the second experiment the vital air combines at first with the inflammable gas, so that a portion of the sulphur is precipitated and can be changed into vitriolic acid only by the addition of a sufficient quantity of dephlogisticated marine acid. It is thus that a part of the sulphur is deposited in the combustion of hepatic gas.

M. DE MORVEAU says, that having mixed and agitated nitrous gas with dephlogisticated marine acid in the mercury apparatus, there was an absorption of about the fifteenth of the volume. He says also (*page* 255, *Dict. de Chim.*) that when this acid is in the state of liquid it does not absorb nitrous gas even when they are kept in contact for a whole month (*ibid.*, *page* 263). I will in the first place remark that, as both dephlogisticated marine acid and the nitrous acid which is formed attack mercury, this apparatus is not suitable for determining the action of dephlogisticated marine acid and nitrous gas, and I have observed that nitrous gas is really decomposed and changed into nitrous acid by dephlogisticated marine acid in the liquid form; but it is mostly in the state of gas that I have examined their reciprocal action. I mixed four measures of nitrous gas with two measures of dephlogisticated marine acid gas, a considerable redness was produced, and the mixture was reduced to 1.4 measure. By employing the calculation of M. LAVOISIER, who fixes the ratio of nitrous gas to vital air, in the composition of nitrous acid, as 69 : 40, we may conclude that the two measures of dephlogisticated marine acid contained 1.507 of vital air, which would seem to indicate that this gas has a considerable specific gravity, to contain so much vital air However, I have not confidence in this result, because nitrous gas dissolves easily in aqua regia, as I have shewn in my Memoir on *aqua regia*, and consequently a part of the nitrous gas could have been abstracted without having really combined with vital air.

Four measures of nitrous gas, or 400 parts, were reduced to 0.35 on passing into it much dephlogisticated marine acid gas, and then absorbing the excess by water.

M. DE MORVEAU adds (*ibid.*, *page* 251) that dephlogisticated marine acid, after having been mixed and agitated with inflammable gas in different proportions, no longer destroyed colours, that it changed blue paper to red, that it had only a very feeble odour, and that thereafter the inflammable gas was found detonating.

Here again I have not been fortunate in obtaining the same results as this celebrated chemist on this subject; I passed into a measured quantity of very pure inflammable gas, several times in succession, an equal volume of dephlogisticated marine acid gas which did not contain atmospheric air; I agitated the mixture each time over water; the absorption of the marine acid gas having been made, the volume of the inflammable gas was not found changed. I then examined this inflammable gas with VOLTA's eudiometer. It was not detonating; I mixed it with vital air, and on detonation it destroyed quite as much as an equal quantity of the same gas which had not been agitated with dephlogisticated marine acid. As I have repeated this experiment several times, I am forced to believe that dephlogisticated marine acid has no action on inflammable gas when it is in the gaseous state, just as vital air in the elastic state has none on marine acid I assured myself of this latter fact by a direct experiment, though it is sufficiently convincing to observe that marine acid does not at all assume the properties of dephlogisticated marine acid when it is left exposed to atmospheric air, of which about a quarter is vital air.

BERGMAN affirms that phosphorus is decomposed by the gas of dephlogisticated marine acid. M. DE MORVEAU and M. ANGULO, on the contrary, have made several experiments by which they claim to prove that phosphorus has no action on dephlogisticated marine acid. I observed, like them, that phosphorus had no action on dephlogisticated marine acid in the cold, and if heat is employed without light, the dephlogisticated marine acid is disengaged in the form of gas, without suffering decomposition; but if a morsel of phosphorus is put into dephlogisticated marine acid and exposed to light, the colour of the acid is dissipated, its odour disappears, the liquid reddens blue vegetable colours, and lime water precipitates calcareous phosphate from it; so that phosphorus combines with the vital air of dephlogisticated marine acid, and becomes phosphoric acid.

Phosphorus, which is exposed to light in dephlogisticated muriatic acid, becomes white and opaque before changing into phosphoric acid; it appears that this state is due to a portion of vital air, which is insufficient to give it the properties of an acid; it is probably thus that phosphorus whitens on the surface when it is preserved for a long time in water; when it is entirely in this state it could be compared to sulphurous acid relatively to vitriolic acid, only that has not yet sufficient vital air to be sensibly acid. It is probably phosphorus thus combined with a portion of vital air which M. de Morveau has called the *acidifiable base of phosphorus*, which he obtained by exposing phosphoric acid in a crucible to a considerable degree of heat; for the portion of vital air which was least adherent to the acid, has been forced to dissipate itself, and there was bound to remain a combination of phosphorus and a little vital air, which is less combustible and less liable to be attacked by nitrous acid 1°, because the affinity of the phosphorus for vital air is already satisfied in part, 2°, because the heat which would be disengaged at the commencement, when the combination took place with the greatest force, cannot in this case aid that part of the combination which takes place only through a feeble affinity. It is thus that sulphur is immediately reduced to vitriolic acid if the combustion is vivid; but that, if the combustion is slow, only sulphurous acid is formed, which then assumes the state of vitriolic acid with some difficulty. It is probable that ordinary phosphoric glass similarily retains a greater or less quantity of vital air.

Chemists in general have believed that all the colours of bodies are due to the same principle diversely modified and combined in different proportions. Bergman in particular has attributed them to phlogiston (Mem. sur l'indigo) and he has claimed to prove by ingenious experiments that the different proportions of this principle cause the variations of colours: thus nitrous acid, which, according to him, is yellow when it has an excess of phlogiston, becomes green if water is added to it, and then blue on further diluting it. The different proportions of vital air which it is here necessary to substitute for phlogiston have a great influence on colours, as the following experiments go to prove; nevertheless nothing in general can be concluded with regard to it, for vital air gives a yellow colour to marine acid, whilst if the proportion in nitrous acid be diminished, this likewise becomes coloured yellow; for it is by driving off vital air that this acid is coloured by light, as I have assured myself by experiments which I have described elsewhere (*Journal de physique*).

The calces of iron, as may be seen in KIRWAN'S Elements of Mineralogy, and may be verified by exposing to the air a precipitate obtained from martial vitriol by fixed alkali, pass through the following gradations according as they are, as he says, more or less dephlogisticated; blue, green, brown, red, yellow, whitish. If concentrated dephlogisticated marine acid is used to dissolve iron, it gives with alkali a pale yellow precipitate; if, on the contrary, the same acid diluted with water is put on the metal it takes a blue colour, and the part which dissolves gives with alkali a blue precipitate, which soon passes to green, brown, red, and finally to a bright yellow, according as more dephlogisticated marine acid is added to it; so that the colours depend only on the quantity of vital air which unites with the iron, and it is now known that martial ethiops only differs from the other calces of iron in that it contains less vital air.

If a solution of copper is precipitated by means of volatile alkali, dephlogisticated marine acid promptly gives to the blue precipitate which has formed, a green colour similar to that which it would take if it was left a long time exposed to air.

Not only does dephlogisticated marine acid destroy vegetable colours, so that alkali cannot restore them, but this effect equally takes place even when a quantity of alkali proper for the saturation of the disguised marine acid is put into the liquid. Among the vegetable colours that of violet syrup is destroyed instantly, likewise that of litmus; but with this latter there remains a yellow tint which resists for some time the action of the liquid; the same thing takes place with the colouring part of Pernambuco wood, and especially with that of madder. Dephlogisticated marine acid loses its properties by acting on the colouring matters, and it resumes those of marine acid, so that the colouring matters combine with the vital air and remove it from the marine acid; they thereby become soluble, but some only by means of the acid so that they can be precipitated by an alkali; others, on the contrary, are soluble in water and are not precipitated by alkali.

The green parts of plants are sometimes reduced to white by dephlogisticated marine acid, at other times to yellow; sometimes they take a reddish colour, in fact they undergo quickly changes perfectly analogous to those which air produces on them naturally; the leaves of evergreen trees resist for a long time the action of dephlogisticated marine acid, and finally take in it only the yellow tint which the air can give them.

The alterations which air produces on colours depend then principally on the vital air combining with them more or less easily, and in quantity more or less considerable; and dephlogisticated marine acid can shew in a few moments the effects which air would only produce in a long space of time: thus, whilst it destroys in a moment the greater number of vegetable colours, to destroy the colour of indigo it requires to act during several days, and a considerable quantity of it is necessary. I shall avail myself of this means of analysis with much more detail to determine the properties of colouring matters which are employed in dyeing, and endeavour to make of the properties of dephlogisticated marine acid some applications useful to the arts.

The action of this liquid appeared to me suitable to give us information as to what happens when plants deprived of light become sickly and whiten, and to explain why plants exposed to the sun give vital air, according to the beautiful observation of M. INGENHOUZ, and why there is no elastic fluid disengaged when they are in the shade, as M. SENEBIER has proved. The oil which enters into the composition of vegetable matters certainly contains much of the inflammable gas obtainable from water, so that it is very probable that water is decomposed in vegetation, that the vital air which it contained is in part exhaled if the light favours its disengagement, as it does for dephlogisticated marine acid and for nitrous acid, whereas without the aid of this affinity it cannot assume the elastic state; then it combines with the colouring matters if there are any formed, and the plants become white; but when the decomposition of the water is not favoured by light it takes place probably to a much less extent, vegetation languishes, the plants have much less oily and resinous matter, and thereby are even deprived of colouring matters: M. SENEBIER also observed that the sickly plants were less inflammable. This theory can be applied to a great number of the phenomena of vegetation (*Journal de phys. Août 1786*).

But dephlogisticated marine acid, which destroys all vegetable colours more or less easily, acts in a different manner on animal colours; it gives a yellow colour to silk and wool, which are white, and we know that nitrous acid produces a similar effect. It appears then that vital air has the property of combining with animal substances, and turning them yellow by this combination.

I have not spoken in this memoir of the phenomena which volatile alkali presents with dephlogisticated marine acid, because I have detailed them in the analysis of volatile alkali; I will simply remark that when caustic volatile alkali is poured on dephlogisticated marine acid it entirely destroys the colour without producing any precipitate; and if a drop of solution of manganese is added to it a slight blackish precipitate is at once perceived.

After the explanations which I have just given I believe that it will suffice to indicate the replies that might be made to some of the difficulties which the learned chemist of Dijon believed could be solved only on the supposition of phlogiston. Manganese treated with fire gives a large quantity of vital air, it loses thereby a part of its black colour, remaining brown however; it cannot dissolve in an acid without losing part of its air, hence vitriolic acid disengages from it a large quantity of vital air on dissolving it; but, with an acid which has little action on it, it is necessary to add a substance which acts, on its part, by its affinity for vital air; such are sugar, gum, etc. If the acid which dissolves the manganese has itself affinity for the air, whilst one part unites with the manganese another part combines with the air which is disengaged from it, and it is this which takes place when marine acid is treated with this substance.

Let us pause a moment to remark that it is not by a simple affinity that marine acid removes the vital air from the calx of manganese. It is only because a portion of this acid dissolves the manganese and drives from it the portion of vital air which is superfluous to the new compound, that the other portion can unite with this vital air deprived in part of the principle of elasticity, as the acid has only a feeble affinity for it.

The precipitate from solutions of manganese differs from manganese in colour and in properties, because it contains much less vital air, so that it cannot be used to make dephlogisticated marine acid, being deprived of that portion of vital air which could combine with the marine acid. The calx of manganese renders glass red when it is abundantly provided with vital air, this colour is dissipated when the less adherent part of the vital air combines with some carbonaceous body. The black calx loses its colour in the inner flame of the blowpipe, because fixed air is formed by the carbonaceous portion; it resumes it again in the external flame because it suffers a new calcination. Lastly, the regulus of manganese gives inflammable gas with vitriolic acid and with marine acid, because having much affinity for vital air it has the property of decomposing water; with nitrous acid it gives nitrous gas, and it detonates with nitre on account of its affinity for vital air, whereas the black calx cannot detonate because it is already saturated with this principle.

MEMOIR

On the development of the principles of the methodical Nomenclature, read at the Academy, 2nd May 1787.[*]

By M. de Morveau.

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Muriatic acid, from the Latin *muria*, *muriaticum*, had already taken the place of *marine acid* in the writings of some chemists; but it is well known that as an acid it stands apart, as it can take up an excess of oxygen and in this state its acidity appears rather to diminish than to augment, this probably being caused by the oxygen retaining a greater quantity of caloric in the compound. Whatever might be the cause of this phenomenon there is no doubt that it required a denomination appropriate to this particular character which till the present has very improperly been designated in the name *dephlogisticated marine acid.* The expression *oxygenated muriatic acid*, *oxygenated muriates*, appeared to us the most simple and the most conform to the object which we had proposed to ourselves, namely, to express only well verified facts. It is by a close adherence to this rule that we have formed the names of all the other compounds of muriatic acid : corrosive sublimate then becomes *corrosive mercurial muriate*; calomel, *mild mercurial muriate*; the salt produced by the ordinary dissolution of tin in this acid, *muriate of tin*; butter of tin, *sublimed muriate of tin*; Libavius' liquor, *fuming muriate of tin*, etc., etc.

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[*] [Translated from "Methode de Nomenclature chimique, *proposé par* MM. de Morveau, Lavoisier, Berthollet, and de Fourcroy." Paris 1787. Pp. 45-7.]

Analogy leads us to believe that muriatic acid has an acidifiable base, in the same way as carbonic, sulphuric, and phosphoric acids, which equally serves to give a proper and particular character to the product of its combination with oxygen: this substance we ought not to designate otherwise than by the expression muriatic *radical* or muriatic radical principle; so as not to give a name to an unknown substance, and to restrict ourselves to the expression of the only property of it which we know, which is in fact to produce this acid. We have had the same circumspection with reference to all the acids of which our knowledge is no more advanced, and of which it is very possible that in the future the bases will be discovered amongst substances already named.

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ABSTRACT

Of the Memoirs read at the National Institute, from the 7th March 1808 *to the 27th February* 1809.*

By MM. GAY-LUSSAC AND THENARD.

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In our sixth memoir (Institute, 9th January 1809) we endeavour to obtain fluoric acid perfectly pure in order to isolate its radical and re-compose the acid. These researches lead us to a great number of new results, of which some are very remarkable, and give rise to our eighth memoir, which was read on the 27th February at the Institute, and has for its object the nature and comparative properties of oxy-muriatic acid gas and muriatic acid.

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Properties of the metal of potash.

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We have also examined the action of the metal of potash on muriatic gas. At the ordinary temperature this action is very slow; but as soon as the metal is fused there is combustion with disengagement of light, and there result muriate of potash and hydrogen gas: as the quantity of hydrogen collected in this experiment is precisely the same as that which the metal would give in contact with water, and as we know, from the experiments of MM. HENRY and BERTHOLLET that muriatic acid gas contains much water, we may believe that this hydrogen comes from the action of the water of the acid on the metal, and consequently we can from this conclude nothing as to the nature of the acid.

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* [Translated from "Mémoires de Physique et de Chimie, de la Société d'Arcueil," tome ii. Paris, 1809. Pp. 295, 298, 307, 308, 320, 321, 339-358.]

In order to solve this question we would require to have muriatic acid free from water; but this, as will be seen by what follows, we can get only by combining it with other bodies, which then prevent its decomposition: that is why, when we treat calomel or oxymuriatic acid gas with phosphorus, we get a liquor formed of oxygen, phosphorus, and muriatic acid, of which the principal characters are that it is strongly acid, devoid of colour, and very limpid; that it becomes troubled in the course of some days; that on contact with the air it spontaneously inflames absorbent paper which has been saturated with it; that it brings about, suddenly and by itself, the combustion of the metal of potash; finally, that with red-hot iron it forms muriate and phosphide of iron, without the disengagement of any gas other than a little muriatic acid.

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On the properties of fluoric acid, and especially its action on the metal of potash.

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. . . . It is thus proved that this gas* cannot contain water in any form, neither in the hygrometric state nor combined. Ammonia gas is absolutely in the same case, at least as regards combined water. But it is not the same with muriatic acid gas; it does not contain hygrometric water, it is true, but it contains it intimately combined, as MM. HENRY and BERTHOLLET first showed. We have even succeeded, by passing muriatic acid gas at a moderate heat over litharge which had been fused and then reduced to coarse powder, in extracting and collecting this water, which must form about one fourth part of its weight, according to various experiments we have made and which will be reported in the subsequent part of this Memoir.

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* [Fluoric acid gas, *i.e.*, boron fluoride, prepared by heating fluor spar with boric anhydride.]

The other gases do not comport themselves with water like the preceding ones. None of them contains combined water, and all contain hygrometric water. It follows from this that fluoric acid gas,* and probably also ammonia gas, does not contain either hygrometric or combined water, that muriatic acid gas does not contain hygrometric water and contains it combined; and that all the others contain only hygrometric water.

The most striking thing in these results is to find that muriatic acid gas contains water, and that fluoric* and ammoniacal gases do not contain it; and especially to find that muriatic acid gas contains it in such proportions that if it were entirely decomposed by a metal all the acid would be absorbed by the oxide and transformed into metallic muriate. This is exactly what takes place, as we have assured ourselves, when muriatic acid gas is passed slowly and successively through several gun-barrels filled with iron turnings and raised to a red heat.

The more we reflect on all these phenomena the more we see that it is difficult to account for them. Might it not be possible however that oxygen and hydrogen are two of the constituent principles of muriatic acid gas, that they are not present in the state of water, and that this is only formed at the moment when the acid enters into combination with bodies; so that in the muriates it would be quite other than in the state of gas? Whatever may be the case this is certain, that none of the muriates undecomposable by heat, and containing only very little or no water, can be decomposed at a very high temperature either by vitreous acid phosphate of lime or by boracic acid likewise in the vitreous state; that, therefore, in the muriates the acid is held with very great force; and, that if even sulphuric acid were deprived of water, it is very probable that it could not decompose them. . . . .

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* [See note p. 35.]

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On the nature and the properties of muriatic acid and of oxygenated muriatic acid.

We had assured ourselves, while engaged on the decomposition of fluoric acid, that muriatic gas was the only one of all the gases which contained combined water, and this singular exception required us to make new researches to determine whether this water was actually essential to its intimate constitution. We first of all sought to determine the quantity of water which could be extracted from muriatic gas, and we got at this in various ways. We dissolved 27.151 grams of muriatic gas in water, cooled to – 20°, and precipitated by means of nitrate of silver. The muriate which resulted therefrom weighed 106.82 grams, representing 20.61 grams of dry acid, seeing that muriate of silver is composed of

100.00	silver
7.60	oxygen
25.71	acid,

consequently, the 27.151 grams of muriatic acid contained 6 54 grams of water, or 0.240 of its weight. This quantity of water contains very nearly enough oxygen to produce the oxide necessary for the saturation of the acid combined with it; for in muriate of silver, of which we have given the proportions, oxygen is to acid as 1 : 3.38; and in muriatic gas the ratio is that of 1 to 3.53.

In order to verify this result, we passed a current of muriatic gas over well-cleaned iron turnings at a dull red heat. Much hydrogen gas was disengaged, without sensible admixture of muriatic gas; much muriate of iron was at the same time obtained; the residual turnings were not oxidised, which proves that the muriatic gas contained exactly enough water to oxidise all the iron which it could dissolve. Consequently, from this result and the ratio of oxygen to silver in muriate of silver, muriatic acid must contain 0.251 of its weight of water.

Again, on decomposing oxygenated muriatic gas by ammoniacal gas, it is found to contain exactly the half of its volume of oxygen gas, and that consequently it can absorb an equal volume of hydrogen. It is further found that a mixture, in equal parts, of oxygenated muriatic gas and hydrogen gas changes, in the course of several days, into ordinary muriatic gas, and that no water is deposited. But as the specific gravity of oxygenated muriatic gas is, according to our experiments, 2.470, that of air being taken as unity, it follows that, on taking away the weight of a half part of oxygen, 0.5517, and adding to this the weight of one part of hydrogen, 0.0753, to form water, a quantity of muriatic acid represented by 2 470 + 0.0732 = 2.5432 contains . . . . 0.5517 + 0.0732 = 0.6249 of water, or 0.2457 of its weight. This quantity differs little from the two preceding, so that we may conclude that ordinary muriatic gas contains 0.25 of its weight of water.

These results show that muriatic gas contains enough water to oxidise the metals which it can dissolve. It would not be possible, or at least it would be very difficult, to decompose it directly. It is for that reason that, without losing the hope of decomposing it, we sought to extract it from oxygenated muriatic gas, by removing the oxygen by means of combustible bodies, as we had found that oxygenated muriatic gas does not contain combined water.

It is not possible to make use of the metals, seeing that with oxygenated muriatic acid they form neutral muriates. It seemed that the sulphides should accomplish our purpose; but, on bringing them into contact with oxygenated muriatic gas, in place of muriatic acid we obtained the sulphur liquor discovered by Mr THOMSON. The sulphites of baryta and of lime did not give us any more satisfactory results; when they were slightly moistened the oxygenated muriatic acid was certainly decomposed; but much sulphurous acid gas was disengaged. When, on the contrary, they were perfectly dry, there was no action. Neither does phosphorus separate oxygen from oxygenated muriatic gas; they combine directly, and form the liquid which we discovered by distilling phosphorus with muriate of mercury.

Finally, as a last method, we tried to decompose oxygenated muriatic gas by charcoal ignited at the extreme heat of the forge. To avoid the presence of the smallest quantity of water we made the gas pass slowly through a large glass tube a meter and a half in length, filled with muriate of lime. This tube communicated with a porcelain tube in which the charcoal was exposed to a red heat. The first portions of the oxygenated muriatic gas were completely converted into ordinary muriatic gas. This effect diminished gradually in spite of a very great elevation of temperature, and soon the gas passed without alteration, mixed only, towards the end of the experiment, with one thirty-third of an inflammable gas, which we believe to be carbonic oxide gas. This result clearly showed us that oxygenated muriatic gas is not decomposed by charcoal, and that the muriatic gas which we had obtained at the commencement of the operation was due to the hydrogen of the charcoal, which had combined with the oxygen of the acid. In fact, on taking ordinary charcoal without igniting it, muriatic gas was disengaged during a lengthened period even at a temperature only slightly elevated, and this acid contained water, like that coming from the decomposition of muriate of soda by sulphuric acid. According as the charcoal lost its hydrogen, however, the quantity of muriatic acid went on diminishing, and finally nothing was obtained but oxygenated muriatic gas. Even plumbago changed the latter gas into ordinary muriatic gas, that is to say, muriatic acid containing water; and since the most strongly ignited charcoal produces the same change, we must conclude that it is the hydrogen gas contained in these bodies which is the true cause of the change. Oxygenated muriatic gas may thus be considered the most powerful agent that we know for depriving charcoal of its hydrogen, seeing that it demonstrates its presence even after the charcoal has been urged to the most violent heat of the forge.

After that we concluded that muriatic acid could not exist without water in the state of gas, and that oxygenated muriatic acid could not be decomposed except by bodies which contain hydrogen, or by those which, like the metals, sulphur, or phosphorus, can form triple compounds with it. New experiments confirmed us in this opinion. We found that dry oxygenated muriatic gas was not decomposed by sulphurous gas, nitrous oxide gas, carbonic oxide gas, or even by nitrous gas, provided that they also were perfectly dry; and that it was decomposed instantly by these same gases with the help of water. Only nitrous gas when mixed with oxygenated muriatic gas slightly altered its colour, changing it to a slightly orange green; but this we doubt not should be attributed to a little water or oxygen, as we had remarked that the drier and purer these two gases were, the less marked was the change of colour.

We know, on the authority of M. BERTHOLLET, that liquid oxygenated muriatic acid is decomposed by light, and, according to M. FOURCROY, that in the state of gas it is not decomposed by this agent, or even by a very high temperature. These facts manifestly prove that the affinity of water for muriatic acid co-operates in this decomposition, and they led us to try the decomposition of oxygenated muriatic gas by means of heat along with water. We therefore arranged an apparatus enabling us to introduce oxygenated muriatic acid gas, alone or mixed with the vapour of boiling water, into a porcelain tube exposed to a red heat. In the first case the gas did not suffer any alteration; but as soon as the vapour of water was introduced oxygen gas and muriatic acid were obtained. It is not necessary for this decomposition that the temperature should be very high, as it still takes place below a red heat.

The affinity of muriatic acid for water is such as to cause the decomposition of oxygenated muriatic gas by hydrogen gas at a temperature only a little higher than that of boiling water. If a mixture of equal parts of these two gases is made and a small piece of iron heated in mercury to 150° introduced, there is a violent inflammation, and formation of muriatic acid.

Here, then, we have a body, oxygenated muriatic gas, which is decomposed neither by light nor by heat, but which, on the other hand, is decomposed quite easily by the one or the other with the help of water. On comparing the action of these two fluids, one cannot but admit that it is identical in every case when it is exercised upon unorganised bodies. M. RUMFORD drew the same conclusion from his experiments on the decomposition of solutions of gold and of silver by charcoal, ether, and oils, by means of light and heat; but the decomposition of oxygenated muriatic gas, which it had not been possible to effect by heat, appeared then a very powerful objection. This exception had not escaped M. BERTHOLLET in his Statique Chimique, and he had added to it another which he had deduced from the difference in the action of heat and of light on nitric acid; he had, however, none the less considered their action as in general identical on almost all other bodies. Our experiments destroy these two objections, and no doubt can remain that light acts on unorganised bodies in the same manner as heat. It is enough even, in order to form a conception of the effects of the former, to admit with M. RUMFORD that it raises the temperature of the molecules on which it acts, while that of the substance in which these molecules may happen to be receives only a slight augmentation.

The decomposition of oxygenated muriatic gas by light is progressive, as it depends on the intensity of the latter. This observation suggested to us that, in a great number of cases in which compounds were formed only slowly, this arose from the fact that they were produced by an agent such as light which, in a very short time, could produce only very small effects, being in small quantity, but which, by being renewed unceasingly, produced very great effects. For it must be admitted that it would be difficult to account otherwise for the slow action which two gases mutually exercise upon one another when in uniform mixture. Since their combination does not take place immediately they are mixed, and since it proceeds thereafter slowly, it is no longer brought about by their mutual affinity; it is due to a foreign cause which assists this affinity, such as light, heat, or electricity even.

Acting on these conjectures we made two mixtures, each consisting of about ½ litre of muriatic gas with the same volume of hydrogen gas, which we knew acted only slowly on one another; one of them we placed in complete darkness, and exposed the other to the light of the sun, which was that day very feeble. At the end of several days the first mixture was still coloured green, and appeared to have undergone no change; the second, on the contrary, had been completely decolourised in less than quarter of an hour, and was almost entirely decomposed. Being no longer able, after these experiments, to doubt as to the influence of light on the combination of the two gases, and judging from the rapidity with which it had operated, that if the light had been much more vivid it would have operated much more quickly, we made new mixtures, both of hydrogen gas with oxygenated muriatic gas and of the latter with olefiant gas, and placed them in complete darkness, awaiting some moments of bright light. Two days after having made the mixtures, we were able to expose them to the sun. Scarcely had they been exposed when they suddenly inflamed with a very loud detonation, and the jars were reduced to splinters, and projected to a great distance. Fortunately we had provided against such occurrences, and had taken precautious to secure ourselves against accident. Compound hydrogen gases would, without doubt, produce the same effect; but carbonic oxide gas placed in the same circumstances does not produce any alteration on oxygenated muriatic gas; a new proof that it does not contain hydrogen.

It is evident then, from these experiments, that it is light which effects the decomposition of oxygenated muriatic gas when it is mixed with hydrogen gas or with compound hydrogen gases. It is at least probable that, in all cases of slow and progressive action between bodies perfectly mixed, light has a very marked influence which doubtless extends also to the decomposition of animal and vegetable matters left to themselves. The action of light on colouring matters would doubtless be the same as that of a heat of 150° to 200°, and it would be interesting to prove that it is so.*

Again, it is quite possible that light acts on plants only as heat, with this great difference however, that heat would raise indifferently the temperature of all the particles which compose the plant, whilst light, by acting on certain particles rather than on others, just as on liquid oxygenated muriatic acid, produces an inequality of temperature doubtless very favourable to the play of the organic forces. One thing which tends to prove this is that in plants it is only the green matter which decomposes carbonic acid. This is a new point of view, from which the chemical affinities have been, as yet, but slightly studied, and we should expect important results from it, by a comparison of the action of bodies placed in darkness with that which they exercise on exposure to light.

The experiments which we have reported up till now ought to give an idea of the constitution of oxygenated muriatic gas quite different from that which had been formed of it. It had been regarded as a most easily decomposed body, and we see, on the contrary, that it resists the action of the most energetic agents, and that it is only with the help of water or of hydrogen that muriatic acid can be extracted from it in the state of gas.

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* Since the reading of this Memoir we have learned that light actually does act on colouring matters in this way.

We had previously discovered that dry muriates could not be decomposed by vitreous boracic acid; but seeing from our experiments that muriatic acid could not be obtained in the gaseous state except with the help of water, we again took up these decompositions with the introduction of the action of this liquid and carried them out very easily.

We first mixed ordinary charcoal with fused muriate of silver, and exposed them to heat in a glass tube closed at one end. Before the tube became red there were disengaged abundant vapours of muriatic gas, and the silver was found reduced. We then ignited some charcoal at the most violent forge-heat which we could produce, and put ten grams of it into a porcelain retort with twice as much fused muriate of silver. When the retort was red we obtained a little muriatic acid, and an inflammable gas burning with a blue flame; but though we increased the heat to the point of destroying the retort, only 3 grams of muriate of silver were decomposed; for all the acid collected and precipitated produced only that quantity of muriate, and we found nearly all the remainder in the retort. Strongly ignited plumbago give us similar results. The decomposition of muriate of silver by charcoal and plumbago forced to the greatest heat having been incomplete, whilst ordinary charcoal, which retains much hydrogen, effects it completely, we must conclude that it is to the hydrogen, retained by the charcoal and plumbago even at the highest temperature, that we must attribute the muriatic gas which we obtained, and that pure carbon could not decompose muriate of silver. Muriate of mercury behaves like this latter; but its volatility does not allow of exposing it to such high temperatures with charcoal.

Finally, seeing from these results that muriatic acid was not disengaged except when the water necessary for its gaseous constitution could be formed, we put fused muriate of silver and strongly ignited charcoal into a glass tube communicating with and luted to a retort containing water. The temperature having been raised to red heat, the salt was not decomposed so long as no water vapour was passed; but the moment the water began to boil, muriatic gas was disengaged very abundantly, and the decomposition of the muriate was complete in a short time. By adding only the quantity of charcoal necessary to reduce the oxide, the silver collects very well, and we do not doubt, from the great facility with which the operation takes place, that this process can be employed on the large scale in working muriate of silver ores. This salt is decomposed by means of water, even without the assistance of charcoal, but then the oxide combines with the glass and colours it yellow. Vitreous boracic acid does not decompose either fused muriate of silver, or that of baryta, or that of soda, whilst, if vapour of water is made to pass, at a red heat, over a mixture of one of these salts and boracic acid, muriatic gas is disengaged very abundantly and borates are formed.

These experiments proving that water contributes very powerfully to the disengagement of muriatic acid, we no longer doubted that it was possible to decompose muriate of soda by water, through aiding its action by that of a body which could unite with the soda. We, therefore, made a mixture of two parts of white sand with one of salt and exposed it to a red heat in a porcelain tube. In this case the salt was not decomposed, but on passing a current of steam through the tube the acid was instantly disengaged in dense and very irritating fumes, and there remained in the tube a vitreous frit of soda and silica. Alumina gives results similar to those with silica; when it is perfectly dry it does not decompose salt, but with the help of water it easily disengages muriatic acid. These experiments promise happy applications, as, in giving a precise idea of the constitution of muriatic gas, they indicate the means which ought to be employed to decompose muriate of soda directly.

On seeking for the bases which could be presented to the soda to separate it from salt by means of water, we had at first thought that carbonic acid would accomplish our object, as the sub-carbonate of soda is not decomposed by heat; but we were very little satisfied with the results which we obtained. We found, in fact, that not only the sub-carbonate of soda, but also the carbonate of baryta, which cannot be decomposed by heat alone, are both decomposed with the help of water. That of lime is in the same case as the preceding; for it loses its acid by heat more easily when the action of water is made to assist. Several of these facts were known, but there was no clear idea of the manner in which they were produced, for it was even supposed that gases could produce the same effects as steam.

We cannot, as with muriatic acid, explain the disengagement of carbonic acid by water, by saying that this liquid is necessary to its gaseous constitution; for carbonic gas does not contain water, and it can quite well be disengaged from certain dry compounds, such as the carbonates of lime and lead, by heat alone; it must consequently be the affinity of water for bases which favours the disengagement of the carbonic acid.

This action of water for acids or for bases is thus much more powerful than has up till now been believed. This it is which determines the formation of sulphuric acid from sulphurous gas and oxygen gas or nitrous gas, and that of nitric acid from this latter gas and oxygen, as M. HUMBOLDT has shown. It is again this action of water which aids the decomposition of nitrate of potash by means of clay; and it is very well known in the establishments where this decomposition is carried out on the large scale, that to obtain a large yield of acid it is necessary to employ very moist clays: when they are too dry only a very little is obtained; the acid is much more concentrated, it is true, but it comes then to too high a price. The same is the case in the decomposition of muriate of soda by clay: which takes place only by means of the water which the latter contains, and stops as soon as this is all evaporated. If certain earthy muriates have been successfully decomposed by heat, this again is only because they contain water. Thus, under whatever circumstances it is sought to obtain muriatic gas, it is only possible to succeed with the help of water. Several other acids, such as sulphuric acid and nitric acid, cannot exist in their state of greatest concentration without water, which appears to be the bond which unites their elements; but water plays a much more important part in muriatic acid. In fact, oxygenated muriatic acid is not decomposed by charcoal, and it might be supposed, from this fact and those which are communicated in this Memoir, that this gas is a simple body. The phenomena which it presents can be explained well enough on this hypothesis; we shall not seek to defend it however, as it appears to us that they are still better explained by regarding oxygenated muriatic acid as a compound body.

EXTRACT FROM
"RECHERCHES PHYSICO-CHIMIQUES"

BY

MM. GAY-LUSSAC AND THENARD

(Paris, 1811. Vol. ii., p. 262).

Table of Facts admitted by the Authors, and contested by Davy.

MM. Gay-Lussac and Thenard's Views.	Davy's Views.
* * *	* * *
Muriatic gas contains the fourth of its weight of water or of the principles of water, and contains no more than this.	Davy is led to believe that muriatic gas contains the third of its weight of water.*
We believe that oxymuriatic gas is a compound of oxygen and another body.	Davy is led to believe that it is a simple substance.
We regard the liquor which is obtained by heating calomel with phosphorus as a triple compound of dry muriatic acid, oxygen, and phosphorus, and as analogous to that which is obtained with sulphur and oxymuriatic acid.	Davy regards this liquor as a compound of oxymuriatic acid (a simple substance) and phosphorus.
* * *	* * *

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* Since Davy published this opinion he has announced another, according to which he regards muriatic acid as composed of oxymuriatic acid (a simple substance) and hydrogen.

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No.

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RESEARCHES
ON THE
MOLECULAR ASYMMETRY
OF
NATURAL ORGANIC PRODUCTS

BY

LOUIS PASTEUR
Membre de la Société Chimique de Paris
(1860)

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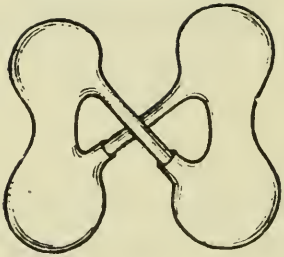

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PREFACE.

THE two Lectures which compose this volume were published by the Chemical Society of Paris in a volume entitled "Leçons de Chimie professées en 1860" (Paris, 1861). They give in brief form an account of Pasteur's brilliant investigations on optically active compounds, and are remarkable for three things :—The fact that they describe the only ways even now known of separating optical isomers : that they contain scarcely a statement which would be changed if they were to be written to-day : and that in the theoretical speculations as to the cause of the difference between optical isomers so close an approach is made to the theory of van't Hoff and Le Bel (1874), that it seems incredible that many years elapsed before the final step was taken.

Two short paragraphs addressed especially to the Chemical Society of Paris and to its president, Dumas, have been omitted from the introduction.

The thanks of the Club are due to the Council of the Society for permission to publish this translation.

A. S.

INTRODUCTORY.

The following Lectures were given at the invitation of the Council of the *Société Chimique* of Paris. The researches of which they form a short summary have occupied my time during ten consecutive years. The thought has often occurred to me to bring together my papers, and, reviewing the details with care and with broader survey, to give co-ordination to the collection of separate memoirs. But in the life of every man who devotes himself to experimental science there comes a stage when the value of time is inestimable; a period of activity when the spirit of discovery is paramount, and when every year should chronicle some advance. To rest on our oars with what is already acquired is annoying and even dangerous, and the harm more than neutralises the pleasure or even the utility of seeing our ideas diffused abroad to the extent of our wishes.

The reluctance which I have felt to undertake the wearisome task of collecting and reviewing my researches on the molecular asymmetry of organic products occurring in nature, has only been equalled by the eagerness with which I acceded to the request of several members of the *Société Chimique*, that I should publish the two Lectures in which the principal results of my work have been explained. Few memoirs have had a better reception than mine, as they have appeared one after the other, and yet I have had many proofs that they are little known.

On this account, I trust that the present publication will be of some use. Besides, if it were only for the interest which the Lectures excited in the select assembly before which they were given, I should feel sufficiently repaid for my pains.

* * * *

L. PASTEUR.

Paris, 1860.

FIRST LECTURE.

I.

AT the end of the year 1808, MALUS announced the discovery that the light reflected by all objects, whether opaque or transparent, acquired new properties of a very extraordinary character, which distinguished it essentially from the light sent to us directly from luminous bodies.

MALUS gave the name *polarisation* to the change which the light underwent in the process of reflection. Later, the expression *plane of polarisation* was used to designate the plane of reflection, that is to say, the plane containing the incident ray and the normal to the reflecting surface.

MALUS' discoveries in connection with polarised light were not limited to this. It had long been known that a ray of direct light was always separated into two beams of white light, of equal intensity, in its passage through a rhomboid of calcium carbonate. Thus the flame of a taper viewed through such a rhomboid is always double, and the two images are equally bright.

HUYGENS and NEWTON had already noticed that light, after its passage through a crystal of Iceland spar, no longer behaves like direct light. Thus, when we study one or other of the images of the taper, just mentioned, through a second rhomboid, we observe (1) that there is not always bifurcation of the ray; (2) that when bifurcation does take place, the two new images have not the same intensity. So that the light which has traversed a doubly refracting crystal is different from ordinary or direct light. Assuming this, MALUS showed that the change produced in light by double refraction was identical with that arising during reflection from the surfaces of opaque or transparent bodies; in other words, that the two rays, ordinary and extraordinary, given by doubly refracting crystals, were polarised rays.

From the first MALUS established these fertile discoveries so clearly, using so much care and precision, both as regards fact and expression, that one would think in reading them that his memoirs had been written yesterday. But he was prevented from continuing his work, having been cut off prematurely in 1812, at the age of 37. Happily for science, two celebrated physicists, BIOT and ARAGO, at that time young and full of activity, took up the legacy he had bequeathed, and speedily distinguished themselves by brilliant discoveries in the new path opened to science by MALUS.

In 1811, ARAGO noticed that, when a ray of polarised light is analysed by a rhomboid of Iceland spar, after it has traversed, normally to the surface, a section of rock crystal cut perpendicularly to the axis, *it always gives two images* in all positions of the rhomboid; and, further, that these are coloured in complementary tints. When the thickness of the spar does not suffice for complete separation of the rays the image is white where they are superposed.

This experiment showed a two-fold anomaly in regard to the ordinary laws of doubly refracting crystals. All other uniaxial crystals, cut normally to the axis, would have given two white, instead of two coloured images, and in two positions of the analysing rhomboid, separated by an angle of 90°, the two images would have been reduced to one.

ARAGO'S conclusion was that the results of the above experiment are precisely those which should follow if it be assumed that the two differently coloured rays from the incident beam of white light are polarised in different planes on leaving the plate of quartz.

Arago did not continue the study of these striking phenomena, and Biot, from 1813 onward, enunciated the physical laws governing them, carefully isolating them from all those with which they seemed to have been confused by Arago.

Biot produced the polarised ray with light from each of the parts of the simple spectrum separately, and found that the original plane of polarisation was deviated through an angle proportional to the thickness of the plate; that this angle was different for each of the primary colours and increased with the refrangibility according to a fixed law. He also made the exceedingly curious observation that of plates obtained from different crystals of quartz, some deviated the plane of polarisation to the right and others to the left, in each case according to the same laws.

But Biot's most remarkable discovery in connection with this kind of phenomena is undoubtedly that of the deviation of the plane of polarisation produced by a number of natural organic products, such as oil of turpentine, solutions of sugar, of camphor, and of tartaric acid. The first mention of this fact occurs in the bulletin of the *Société Philomatique* for December 1815.

To understand this Lecture it is essential particularly to recollect the existence of this rotative property in tartaric acid, and its absence in paratartaric or racemic acid, an acid isomeric with tartaric acid.

There exist, therefore, organic products which, when themselves liquid, or when dissolved in water, possess the rotative property, and resemble in this respect solid crystallised quartz. But it must be noted here that the analogy with quartz is superficial only. The deviation of the plane of polarisation is common to both, but the character of the phenomenon is quite different.

Thus quartz deviates; but it must be crystallised. Dissolved, or solid and not crystallised, it lacks the property. Not only must it be crystallised, but it must be cut in plates perpendicular to the axis. As soon as the plate is slightly inclined to the direction of the ray, the effect is diminished and finally disappears.

Sugar deviates (and what is said of sugar is true of all the other organic products), but the sugar must be dissolved, or solid and amorphous as in barley-sugar. In the crystallised state it was impossible to discover any effect.

The tube containing the solution of sugar may be inclined. The deviation does not alter for equal thicknesses. And, what is more, active agitation of the liquid by means of clock-work leaves the phenomenon the same.

So that, from the first, BIOT quite definitely concluded that the action produced by the organic bodies was a molecular one, peculiar to their ultimate particles and depending on their individual constitution. In quartz the phenomenon is a consequence of the mode of aggregation of the crystalline particles.

These are the physical precedents, if I may so express myself, for the researches which I am about to lay before you. We must next consider their mineralogical precedents.

II.

Hemihedry is certainly the one of the peculiarities of crystallisation which is most easily grasped in its external manifestation. Consider, for example, a mineral species crystallising in the cubic form. This species can show, as everyone knows, various kinds of forms determined by the law of symmetry, a law so natural that it is, so to speak, a physical axiom. This law states that, if one kind of form is given, all the others compatible with it may be obtained by an artifice which consists in modifying, truncating as Romé de Lisle says, identical parts, simultaneously and in the same manner. Identical edges are such as are formed by the intersection of faces which are severally identical and which cut at the same angle; and identical solid angles are those which are formed by dihedral angles which are identical and similarly placed. Thus in the cube there is only one kind of solid angle and one kind of edge. If one of the angles is truncated by a face equally inclined to the three faces of the solid angle, the other seven angles must be simultaneously truncated by a face of the same nature. This is what we observe in alum, in galena, and, generally, in all cubical species.

Let us imagine a right prism with rhombic base. The eight basal edges are identical edges. If one is truncated, the other seven must be truncated, and in the same manner. The four vertical edges are of another kind. In general, they will not be truncated at the same time with the basal ones, and if they are it will be differently.

These examples will suffice to make clear the law of symmetry and its application.

Nothing is simpler than to have a precise conception of hemihedry. It has long been known—in fact Haüy was acquainted with the most noted examples—that in a crystal sometimes only the half of the identical parts are modified simultaneously, and in the same manner. In such cases hemihedry is said to exist. Thus the cube ought to have its eight solid angles all truncated at once. But in certain cases this only occurs to four of them. Boracite furnishes an example of this nature. In these circumstances the modification takes place in such a way that, if the four truncations are produced so as to obliterate the faces of the cube, a regular tetrahedron is obtained. If the modification were applied to the four remaining angles, it would give rise to another regular tetrahedron, identical with and superposable on the first, and differing from it only by its position on the cube.

In the same way let us again consider our right prism truncated on the eight basal edges. In certain species the truncation takes place on one half only of the edges, and here again the result is that, as the truncations occur on the opposite edges of each base, and alternately at the two extremities, these truncations, if produced, give rise to a tetrahedron. As in the case of the cube, two tetrahedra are possible, differently placed with reference to the prism, according as one or other of the sets of four truncations is preserved; but here the two tetrahedra are not absolutely identical. They are symmetrical tetrahedra. They cannot be superposed.

These notions will be sufficient to enable us to understand what hemihedry is, and what is understood by hemihedral faces or forms.

Now quartz, of which we were speaking a short time ago, is one of the few minerals in which Haüy discovered hemihedral faces. Everybody knows the ordinary form of this mineral, a regular hexagonal prism terminated by two six-faced pyramids. It is evident that the trihedral angles situated at the base of the pyramidal faces are identical, and, therefore, if one of these bears a face, all the others should exhibit the same modification. This is the case with the so-called rhomb-face of the mineralogists.

But Haüy was the first to observe, in certain specimens, a face very different from these, which he designated by the letter *x*, inclined more towards one side than the other, without being double, as the law of symmetry would require in this case. Another strange peculiarity of these crystals did not escape crystallographers, namely, that this face x was inclined sometimes in one sense, sometimes in the other. HAÜY, who liked to give suitable names to each variety of a species, called the variety of quartz bearing the face x *plagihedral.* The crystals in which the face x was inclined to the right, when the crystal was oriented in a given manner, were called right plagihedra; those in which x was inclined in the opposite sense, left plagihedra.

Nothing, however, is more variable than this character. Here it exists, there it is absent. On one and the same crystal there are angles bearing the face x, others which ought to bear it are without it. Sometimes both right and left plagihedral faces are found. Nevertheless, all who were conversant with crystals agreed in admitting that there was in quartz a true hemihedry in two opposite senses.

We should notice here a very ingenious association of ideas, due to Sir JOHN HERSCHEL, which was communicated to the Royal Society of London in 1820.

I have already said that BIOT made the remarkable observation, that among different specimens of quartz some deviated the plane of polarised light in one sense, and the others in the opposite sense, to the right and to the left respectively. This being established, HERSCHEL connected HAÜY'S crystallographic discovery with BIOT'S physical one. Experiment confirmed the idea of an actual relation between right and left plagihedra and the right and left senses of the optical deviations. Specimens of quartz bearing the face x in the same sense, all deviate the plane of polarised light in one sense.

Such is the statement of the principal facts antecedent to the researches of which I am about to give you a short account.

III.

When I began to devote myself to special work, I sought to strengthen myself in the knowledge of crystals, foreseeing the help that I should draw from this in my chemical researches. It seemed to me to be the simplest course, to take, as a guide, some rather extensive work on crystalline forms; to repeat all the measurements, and to compare my determinations with those of the author. In 1841, M. de la Provostaye, whose accuracy is well known, had published a beautiful piece of work on the crystalline forms of tartaric and paratartaric acids and of their salts. I made a study of this memoir. I crystallised tartaric acid and its salts, and investigated the forms of the crystals. But, as the work proceeded, I noticed that a very interesting fact had escaped the learned physicist. All the tartrates which I examined gave undoubted evidence of hemihedral faces.

This peculiarity in the forms of the tartrates was not very obvious. This will be readily conceived, seeing that it had not been observed before. But when, in a species, its presence was doubtful, I always succeeded in making it manifest by repeating the crystallisation and slightly modifying the conditions. Sometimes the crystals bore all the faces demanded by the law of symmetry, but the hemihedry was still betrayed by an unequal development of one half of the faces. This is seen, for example, in tartar emetic. It must be admitted that a circumstance which adds greatly to the difficulty in recognising hemihedry is the frequent irregularities of the crystals, which never develop quite freely. From this cause there arise deformations, arrestments of development in one direction or another, faces suppressed by accident, etc. Unless in circumstances of an almost exceptional character, the recognition of hemihedry, particularly in laboratory crystals, demands very attentive study. To this we must add the fact that, although hemihedry may be possible in a given form, and although it is a function of the internal structure of the substance, it may not be indicated externally, any more than one finds on every crystal of a cubic species all the forms compatible with the cube.

But however these things may be, I repeat that I found the tartrates hemihedral.

This observation would probably have remained sterile, without the following one.

Let a, b, c, be the parameters of the crystal form of any tartrate, and α, β, γ, the angles of the crystallographic axes. The latter are ordinarily perpendicular, or slightly oblique. In addition, the ratio of two parameters, such as a and b, is almost the same in the various tartrates, whatever may be their composition, their quantity of water of crystallisation, or the nature of the bases; c alone shows sensible variations. There is a kind of semi-isomorphism among all the tartrates. One would imagine that the tartaric group dominated and stamped with similarity the forms of all the various substances in spite of the difference in the other constituent elements.

The results of this are, a resemblance in the forms of all tartrates, and the possibility of parallel orientation, taking, for example, as basis of orientation the position of the axes a and b.

Now if we compare the disposition of the hemihedral faces on all the prisms of the primitive forms of the tartrates, when they are oriented in the same manner, this disposition is found to be the same.

These results, which have been the foundation of all my later work, may be summed up in two words: the tartrates are hemihedral, and that in the same sense.

Guided then on the one hand by the fact of the existence of molecular rotatory polarisation, discovered by BIOT in tartaric acid and all its compounds, and on the other by HERSCHEL's ingenious correlation, and yet again by the sagacious views of M. DELAFOSSE, with whom hemihedry has always been a law of structure and not an accident of crystallisation, I believed that there might be a relation between the hemihedry of the tartrates and their property of deviating the plane of polarised light.

It is important thoroughly to grasp the development of the conceptions:—HAÜY and WEISS observe that quartz possesses hemihedral faces and that these faces incline to the right on some specimens and to the left on others. BIOT on his part finds that quartz crystals likewise separate themselves into two sets, in relation to their optical properties, the one set deviating the plane of polarised light to the right, the other to the left, according to the same laws. HERSCHEL in his turn supplies to these hitherto isolated facts the bond of union, and says:—Plagihedra of one kind deviate in the same sense; plagihedra of the other kind deviate in the opposite sense.

For my own part I find that all tartrates are plagihedral, if I may so express myself, and that in the same sense; so that I might presume that here, as in the case of quartz, there was a relation between the hemihedry and the circular polarisation. At the same time the essential differences to which I have just referred between circular polarisation in quartz and in tartaric acid must not be neglected.

Thanks to the above discoveries, and to the relations which I have just enumerated, we are now in possession of a preconceived notion (for it is still nothing more than that) as to the possible inter-relation of the hemihedry and the rotative power of the tartrates.

Being very anxious to find by experiment some support for this still purely speculative view, my first thought was to see whether the very numerous crystallisable organic products which possess the molecular rotative property, have hemihedral crystalline forms, an idea which had not previously occurred to any one in spite of HERSCHEL'S correlation. This investigation met with the success which I anticipated.

I also occupied myself with the examination of the crystalline forms of paratartaric acid and its salts. These substances are isomeric with the tartaric compounds, but had all been found by BIOT to be inactive towards polarised light. None of them exhibited hemihedry.

Thus the idea of the inter-relation of the hemihedry and the molecular rotatory power of natural organic products gained ground.

I was soon enabled to establish it clearly by a wholly unexpected discovery.

IV.

I must first place before you a very remarkable note by MITSCHERLICH which was communicated to the *Académie des Sciences* by BIOT. It was as follows:—

"The double paratartrate and the double tartrate of soda and ammonia have the same chemical composition, the same crystalline form with the same angles, the same specific weight, the same double refraction, and consequently the same inclination in their optical axes. When dissolved in water their refraction is the same. But the dissolved tartrate deviates the plane of polarisation, while the paratartrate is indifferent, as has been found by M. BIOT for the whole series of those two kinds of salts. Yet," adds MITSCHERLICH, "*here the nature and number of the atoms, their arrangement and distances, are the same in the two substances compared.*"

This note of MITSCHERLICH'S attracted my attention forcibly at the time of its publication. I was then a pupil in the *École Normale*, reflecting in my leisure moments on these elegant investigations of the molecular constitution of substances, and having reached, as I thought at least, a thorough comprehension of the principles generally accepted by physicists and chemists. The above note disturbed all my ideas. What precision in every detail! Did two substances exist which had been more fully studied and more carefully compared as regards their properties? But how, in the existing condition of the science, could one conceive of two substances so closely alike without being identical? MITSCHERLICH himself tells us what was, to his mind, the consequence of this similarity:

The nature, the number, the arrangement, and the distance of the atoms are the same. If this is the case what becomes of the definition of chemical species, so rigorous, so remarkable for the time at which it appeared, given by CHEVREUL in 1823? *In compound bodies a species is a collection of individuals identical in the nature, the proportion, and the arrangement of their elements.*

In short, MITSCHERLICH'S note remained in my mind as a difficulty of the first order in our mode of regarding material substances.

You will now understand why, being preoccupied, for the reasons already given, with a possible relation between the hemihedry of the tartrates and their rotative property, MITSCHERLICH'S note of 1844 should recur to my memory. I thought at once that MITSCHERLICH was mistaken on one point. He had not observed that his double tartrate was hemihedral while his paratartrate was not. If this is so, the results in his note are no longer extraordinary; and further, I should have, in this, the best test of my preconceived idea as to the inter-relation of hemihedry and the rotatory phenomenon.

I hastened therefore to re-investigate the crystalline form of MITSCHERLICH'S two salts. I found, as a matter of fact, that the tartrate was hemihedral, like all the other tartrates which I had previously studied, but, strange to say, the paratartrate was hemihedral also. Only, the hemihedral faces which in the tartrate were all turned the same way, were, in the paratartrate inclined sometimes to the right and sometimes to the left. In spite of the unexpected character of this result, I continued to follow up my idea. I carefully separated the crystals which were hemihedral to the right from those hemihedral to the left, and examined their solutions separately in the polarising apparatus. I then saw with no less surprise than pleasure that the crystals hemihedral to the right deviated the plane of polarisation to the right, and that those hemihedral to the left deviated it to the left; and when I took an equal weight of each of the two kinds of crystals, the mixed solution was indifferent towards the light in consequence of the neutralisation of the two equal and opposite individual deviations.

Thus, I start with paratartaric acid; I obtain in the usual way the double paratartrate of soda and ammonia; and the solution of this deposits, after some days, crystals all possessing exactly the same angles and the same aspect. To such a degree is this the case that MITSCHERLICH, the celebrated crystallographer, in spite of the most minute and severe study possible, was not able to recognise the smallest difference. And yet the molecular arrangement in one set is entirely different from that in the other. The rotatory power proves this, as does also the mode of asymmetry of the crystals. The two kinds of crystals are isomorphous, and isomorphous with the corresponding tartrate. But the isomorphism presents itself with a hitherto unobserved peculiarity; it is the isomorphism of an asymmetric crystal with its mirror image. This comparison expresses the fact very exactly. Indeed, if, in a crystal of each kind, I imagine the hemihedral facets produced till they meet, I obtain two symmetrical tetrahedra, inverse, and which cannot be superposed, in spite of the perfect identity of all their respective parts. From this I was justified in concluding that, by the crystallisation of the double paratartrate of soda and ammonia, I had separated two symmetrically isomorphous atomic groups, which are intimately united in paratartaric acid. Nothing is easier than to show that these two species of crystals represent two distinct salts from which two different acids can be extracted.

Using the treatment always employed in such cases, the purpose is served by precipitating each salt with a salt of lead or baryta, and then isolating the acids by means of sulphuric acid.

The study of these acids is of immense interest. I do not know any that is more interesting.

But before enlarging on it allow me to introduce here some recollections in connection with their discovery.

V.

The announcement of the above facts naturally placed me in communication with Biot, who was not without doubts regarding their accuracy. Being charged with giving an account of them to the Academy, he made me come to him and repeat before his eyes the decisive experiment. He handed over to me some paratartaric acid which he had himself previously studied with particular care, and which he had found to be perfectly indifferent to polarised light. I prepared the double salt in his presence, with soda and ammonia which he had likewise desired to provide. The liquid was set aside for slow evaporation in one of his rooms. When it had furnished about 30 to 40 grams of crystals, he asked me to call at the *Collége de France* in order to collect them and isolate before him, by recognition of their crystallographic character, the right and the left crystals, requesting me to state once more whether I really affirmed that the crystals which I should place at his right would deviate to the right, and the others to the left. This done, he told me that he would undertake the rest. He prepared the solutions with carefully measured quantities, and when ready to examine them in the polarising apparatus, he once more invited me to come into his room. He first placed in the apparatus the more interesting solution, that which ought to deviate to the left. Without even making a measurement, he saw by the appearance of the tints of the two images, ordinary and extraordinary, in the analyser, that there was a strong deviation to the left. Then, very visibly affected, the illustrious old man took me by the arm and said :—

"*My dear child, I have loved science so much throughout my life that this makes my heart throb.*"

You will pardon me, gentlemen, these personal recollections which have never been effaced from my mind. In our day, and with our habits, they would offend in a scientific memoir, but they have seemed to me not out of place in an oral account ; and perhaps the biographical interest of such recollections will constitute one of the advantages of the kind of instruction which the *Société Chimique* inaugurates to-day.

Indeed there is more here than personal reminiscences. In BIOT's case the emotion of the scientific man was mingled with the personal pleasure of seeing his conjectures realised. For more than thirty years BIOT had striven in vain to induce chemists to share his conviction that the study of rotatory polarisation offered one of the surest means of gaining a knowledge of the molecular constitution of substances.

VI.

Let us return to the two acids furnished by the two sorts of crystals deposited in so unexpected a manner in the crystallisation of the double paratartrate of soda and ammonia. I have already remarked that nothing could be more interesting than the investigation of these acids.

One of them, that which comes from crystals of the double salt hemihedral to the right, deviates to the right, and is identical with ordinary tartaric acid. The other deviates to the left, like the salt which furnishes it. The deviation of the plane of polarisation produced by these two acids is rigorously the same in absolute value. The right acid follows special laws in its deviation, which no other active substance had exhibited. The left acid exhibits them, in the opposite sense, in the most faithful manner, leaving no suspicion of the slightest difference.

That paratartaric acid is really the combination, equivalent for equivalent, of these two acids, is proved by the fact that, if somewhat concentrated solutions of equal weights of each of them are mixed, as I shall do before you, their combination takes place with disengagement of heat, and the liquid solidifies immediately on account of the abundant crystallisation of paratartaric acid, identical with the natural product.*

In accord with their chemical and crystallographic properties, all that can be done with one acid can be repeated with the other under the same conditions, and in each case we get identical, but not superposable products; products which resemble each other like the right and left hands. The same forms, the same faces, the same angles, hemihedry in both cases. The sole dissimilarity is in the inclination to right or left of the hemihedral facets and in the sense of the rotatory power.

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* This beautiful experiment called forth applause from the audience.

VII.

From these results, as a whole, it is evident that we have to do with two isomeric substances, whose general relations as regards similitude and molecular dissimilarity we know.

Now recall the definition of a chemical species which I gave a few minutes ago:—the aggregate of individuals identical in the *nature*, the *proportion*, and the *arrangement* of the elements. All the properties of substances are functions of these three terms, and the object of all our work is to pass, by investigation of the properties, to the knowledge of these three things.

In isomeric bodies, the nature and proportion are the same. The arrangement alone differs. The great interest of isomerism has been to introduce into the science the principle that substances may be, and are, essentially different solely because the arrangement of the atoms is not the same in their chemical molecules.

But no isomeric bodies existed whose relations in respect to molecular arrangement could be known. This desideratum was supplied for the first time by the discovery of the constitution of paratartaric acid, and of the constitutional relations of the right and left tartaric acids. We know, on the one hand, that the molecular structures of the two tartaric acids are asymmetric, and on the other, that they are rigorously the same, with the sole difference of showing asymmetry in opposite senses. Are the atoms of the right acid grouped on the spirals of a dextrogyrate helix, or placed at the summits of an irregular tetrahedron, or disposed according to some particular asymmetric grouping or other? We cannot answer these questions. But it cannot be a subject of doubt that there exists an arrangement of the atoms in an asymmetric order, having a non-superposable image. It is not less certain that the atoms of the left acid realise precisely the asymmetric grouping which is the inverse of this. Lastly, we know that paratartaric acid results from the juxtaposition of these two inversely asymmetric atomic groupings.

Henceforth the observation of the chemical and physical resemblances and differences, corresponding to these arrangements whose relations are known to us, offers especial interest, and gives solid foundations to molecular mechanics. It enables us to establish the connection of the physical and chemical properties, with the molecular arrangement which determines their very existence, or conversely it enables us to pass from the properties to their primary cause.

A *résumé* of these general relations between the properties and corresponding atomic arrangements may be given as follows:—

(1.) When the elementary atoms of organic products are grouped asymmetrically, the crystalline form of the substance manifests this molecular asymmetry in non-superposable hemihedry.

The cause of the hemihedry is thus recognised.

(2.) The existence of this same molecular asymmetry betrays itself, in addition, by the optical rotative property.

The cause of rotatory polarisation is likewise determined.*

(3.) When the non-superposable molecular asymmetry is realised in opposite senses, as happens in the right and left tartaric acids and all their derivatives, the chemical properties of these identical and inverse substances are rigorously the same. From this it follows that this mode of contrast, and of similarity, does not alter the ordinary play of chemical affinities.

I am in error: there is a restriction to make on this last point, an important and eminently instructive restriction. Time does not permit me to develop it deliberately and suitably to-day. It will find a place in the next Lecture.

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* FRESNEL, with one of those flashes of genius, of which he had so many, had a sort of presentiment of this cause of rotatory polarisation.

He expresses himself thus, in one of his memoirs, in vol. xxviii. of the *Annales de chimie et de physique*, 1825:—"Rock crystal shows optical phenomena which cannot be reconciled with complete parallelism of the molecular lines, and which would seem to indicate a progressive and regular deviation of these lines in the passage from one layer of the medium to the next."

SECOND LECTURE.

I.

WHEN we study material things of whatever nature, as regards their forms and the repetition of their identical parts, we soon recognise that they fall into two large classes of which the following are the characters. Those of the one class, placed before a mirror, give images which are superposable on the originals; the images of the others are not superposable on their originals, although they faithfully reproduce all the details. A straight stair, a branch with leaves in double row, a cube, the human body,—these are of the former class. A winding stair, a branch with the leaves arranged spirally, a screw, a hand, an irregular tetrahedron,—these are so many forms of the other set. The latter have no plane of symmetry.

We know on the other hand that compound substances are aggregates of identical molecules, themselves formed of assemblages of elementary atoms distributed according to laws which regulate their nature, proportion, and arrangement. The individual, for every compound substance, is its chemical molecule, and this is a group of atoms. It is not a confused group: on the contrary, its arrangement is definitely fixed. Such is the view of all physicists in regard to the constitution of substances.

This being granted, it would certainly have been very extraordinary if nature, various in its effects as it is, and exhibiting laws which permit the existence of so many species of substances, had not presented us, among the atomic groups of compound molecules, with both of the categories into which all objects may be divided. In other words, it would have been wonderful if, in the whole range of natural and artificial chemical substances, there had not been individuals with superposable images and others with non-superposable images.

The actual fact is just what might have been foreseen; all chemical compounds without exception likewise fall into two classes,—those with superposable images and those with non-superposable images.

II.

It is easy to show that this is a legitimate consequence forced on us by our former discussion. To put it clearly before us I shall briefly recall the principal conditions of the decisive experiment with which we concluded the preceding Lecture.

I prepare the paratartrate of soda and ammonia from natural paratartaric acid. Beautiful crystals are deposited.

If any part of the solution of the double salt is examined in the polarising apparatus, it exhibits no trace of optical deviation; and if the acid is recovered from the crystals, paratartaric acid, identical with that used at first, is obtained. So far everything is simple and natural, and we would imagine that it was a question of crystallising an ordinary salt. Yet it is not so.

Take another portion of the same crystals and examine them one by one. You will find that half of them have the form, of which I here show a model, characterised by non-superposable hemihedry, and that the other half have the inverse form, identical with the first in all its respective parts and yet not superposable on it. If we then pick out the two sorts of crystals for separate solution, we find that one of the solutions deviates the polarised light to the right, the other to the left, and both to the same extent in absolute value.

Finally, if we extract the acids from these two sorts of crystals by ordinary chemical means, we recognise that one of them is identical with ordinary tartaric acid, and that the other is in all respects similar to it without being superposable on it. They are related to each other in the same way as the salts from which they are obtained. They resemble each other as the right hand resembles the left: better still, they resemble each other like a symmetrical pair of irregular tetrahedra, and these analogies and differences are repeated in all their derivatives. What can be done with one can be done with the other under like conditions, and the resulting products exhibit always the same properties, with the single difference that in the one case the deviation of the plane of polarisation is to the right, in the other to the left, and that the forms of corresponding species, while identical in all their details, cannot be superposed.

All these facts, clear and decisive as they are, compel us to refer the general external characters of these acids and their compounds to their individual chemical molecules. To refuse to do this would be to disregard the most ordinary rules of logic. We thus arrive at the following consequences:—

(1.) The molecule of tartaric acid, whatever else it may be, is asymmetric, and in such a way that the image is not superposable. (2.) The molecule of the left tartaric acid is formed by the exactly inverse group of atoms. And by what characters shall we recognise the existence of molecular asymmetry? On the one hand by non-superposable hemihedry, on the other, and more especially, by the rotatory optical property when the substance is in solution.

These principles being granted, if we examine all the products of nature, or of the laboratory, we shall easily discover that a number of them exhibit at the same time this kind of hemihedry and the molecular rotatory property, and that all the others show neither the one nor the other of these characters.

I was therefore justified in saying that the legitimate and inevitable consequence of our former discussion may be expressed in this way :—

All bodies (I here employ the expression in the chemical sense) fall into two great classes, bodies with superposable images and bodies with non-superposable images,—bodies with asymmetric atomic arrangement and those with homohedral atomic arrangement.

III.

Here we encounter a fact which would be worthy of our attention, even if we considered it alone and separate from the set of considerations which follows. It is this :—

All artificial products of the laboratory and all mineral species are superposable on their images. On the other hand, most natural organic products (I might even say all, if I were to name only those which play an essential part in the phenomena of vegetable and animal life), the essential products of life, are asymmetric, and possess such asymmetry that they are not superposable on their images.

Before going further, I wish to remove some objections which will not fail to arise in your minds.

IV.

Quartz! you will say at once. We saw in the last Lecture that quartz possesses the two characteristics of asymmetry—hemihedry in form, observed by HAÜY, and the rotative phenomenon discovered by ARAGO! Nevertheless, *molecular* asymmetry is entirely absent in quartz. To understand this, let us take a further step in the knowledge of the phenomena with which we are dealing.

We shall find in it, besides, the explanation of the analogies and differences already pointed out between quartz and natural organic products.

Permit me to illustrate roughly, although with essential accuracy, the structure of quartz and of the natural organic products. Imagine a spiral stair whose steps are cubes, or any other objects with superposable images. Destroy the stair and the asymmetry will have vanished. The asymmetry of the stair was simply the result of the mode of arrangement of the component steps. Such is quartz. The crystal of quartz is the stair complete. It is hemihedral. It acts on polarised light in virtue of this. But let the crystal be dissolved, fused, or have its physical structure destroyed in any way whatever; its asymmetry is suppressed and with it all action on polarised light, as it would be, for example, with a solution of alum, a liquid formed of molecules of cubic structure distributed without order.

Imagine, on the other hand, the same spiral stair to be constructed with irregular tetrahedra for steps. Destroy the stair and the asymmetry will still exist, since it is a question of a collection of tetrahedra. They may occupy any positions whatsoever, yet each of them will none the less have an asymmetry of its own. Such are the organic substances in which all the molecules have an asymmetry of their own, betraying itself in the form of the crystal. When the crystal is destroyed by solution, there results a liquid active towards polarised light, because it is formed of molecules, without arrangement, it is true, but each having an asymmetry in the same sense, if not of the same intensity in all directions.

V.

Quartz is therefore not molecularly asymmetric, and up to the present we have not any example of a mineral possessing molecular asymmetry. I have remarked that this proposition must be extended to the artificial compounds of the laboratory. Here again some scruples may be felt. It might be objected, for instance, that natural camphor, which is asymmetric, gives, artificially, camphoric acid, which is likewise asymmetric; that aspartic acid derived from asparagine by a laboratory reaction is asymmetric in the same way as asparagine, and I might cite many other similar examples. But no one can doubt that camphoric and aspartic acids owe their own asymmetry to camphor and to asparagine. This existed in the original products, and is handed on, more or less modified by substitution, from the original substances to their derivatives. In fact, a better proof of the conservation of the primitive type, in a series of products united together by a common origin, than that given by the permanence of the optical property, could not be adduced.

When I affirm that no artificial substance has yet shown molecular asymmetry, I refer to artificial substances properly so called, made entirely of mineral elements or derived from substances not themselves asymmetric. Thus, alcohol is not asymmetric. Its molecule, if we could isolate and study it, when placed before a mirror would give a superposable image. Now not a single derivative of alcohol is asymmetric. I could multiply *ad infinitum* examples of this kind. More than this: take any asymmetric substance whatever, and, if you submit it to fairly energetic chemical reactions, you may confidently expect to see the asymmetry of the primitive group disappear. Thus, tartaric acid is asymmetric. Pyrotartaric acid is not so. Malic acid is asymmetric. The maleic and paramaleic acids of Pelouze are not. Gum is asymmetric, mucic acid is not.

Artificial products have, therefore, no molecular asymmetry; and I could not point out the existence of any more profound distinction between the products formed under the influence of life, and all others. Let us enforce this point more strongly, for you will find the physiological side of these researches become more and more prominent in the remainder of this Lecture. Let us pass in review the prinoipal classes of natural organic products.

Cellulose, starches, gums, sugars,—tartaric, malic, quinic, tannic acids,—morphine, codeine, quinine, strychnine, brucine,—essences of turpentine, of citron,—albumen, fibrin, gelatin. All these immediate principles are molecularly asymmetric. All these substances in the state of solution possess the rotative power, a characteristic necessary and sufficient to establish their asymmetry, even when, crystallisation being impossible, hemihedry is lacking as a means of recognising this property.

All the substances most essential in the animal or vegetable organism appear in this list.

There are many natural substances which are not asymmetric. But are they natural in the same sense as the others? Must we not regard bodies like oxalic acid, hydride of salicyle, fumaric acid, etc., as derivatives of natural substances properly so called, formed by interactions analogous to those of the laboratory? These products appear to me to be, in the vegetable organism, what urea, uric acid, creatine, glycocoll, etc., are in the animal organism—excretions rather than secretions, if I may so speak. It would be very interesting to follow up this point of view experimentally.

Let us add that many substances which are apparently not asymmetric, may be like *paratartaric acid.* We still want a word in chemical language to express the fact of a double molecular asymmetry concealed by the neutralisation of two opposite asymmetries, the physical and geometrical effects of which rigorously compensate each other.

The double proposition to which we have been led, on the habitual asymmetry of immediate organic principles, and on the absence of this character in all the products of inorganic nature, will permit us to enlarge and render more definite our mode of regarding the subject of this remarkable molecular property.

VI.

In 1850 M. Dessaignes, whose ingenuity and skill are known to all chemists, announced to the Academy that he had succeeded in transforming bimalate of ammonia into aspartic acid. This was an advance which confirmed the important results obtained by Piria some years before. Piria had succeded in transforming asparagine and aspartic acid into malic acid. M. Dessaignes, in turn, showed that conversely we could return from malic acid to aspartic acid.

So far everything connected with M. Dessaignes' observation was perfectly natural, even from the optical point of view. For, on my side, I had found that asparagine, aspartic acid and malic acid were active towards polarised light. The passage chemically from one to the other of these bodies had nothing astonishing about it.

A few months later M. Dessaignes took a further step. He announced that not only bimalate of ammonia, but also fumarate and maleate of ammonia had likewise the property of being transformed by heat into aspartic acid.

Here I saw an impossibility; or, if the facts were as M. Dessaignes stated, this skilful chemist had made a discovery which he did not suspect. I had in fact observed that fumaric and maleic acids and all their salts were without action upon polarised light. If, therefore, M. DESSAIGNES had succeeded in transforming their ammonia salts into aspartic acid, he would have accomplished for the first time the production of an asymmetric substance by the aid of compounds which are not so.

But it seemed to me more reasonable to suppose that the aspartic acid of M. DESSAIGNES differed from natural aspartic acid in the absence especially of the molecular rotatory property. M. DESSAIGNES, it is true, had carefully compared the properties of the artificial acid with those of the natural acid, and stated that he had found them identical. After the example of MITSCHERLICH, of which I spoke in last Lecture, I knew better than anyone else what delicate things were the demonstrations of the identity of chemical species, in investigations where the greatest similarity in properties often conceals profound differences. I had therefore no hesitation in believing that the new fact reported by M. DESSAIGNES required confirmation.

Attaching so much importance to the elucidation of this question, and indeed foreseeing the results which I am about to have the honour of explaining to you, I immediately set out for Vendôme, where I related my suspicions to M. DESSAIGNES, and he hastened to supply me with a specimen of his aspartic acid. As a matter of fact I found, as soon as I reached Paris, that M. DESSAIGNES' acid was only an isomer of natural aspartic acid, that is of the acid from asparagine. It differed from it, as I had foreseen, in the rotatory property, which was quite absent in the artificial acid and indubitable in the natural acid. Yet all the other chemical and physical properties showed the greatest analogies, so great that

M. Dessaignes, not being put on his guard by any preconceived idea, had decided that the two substances were really identical.

What charmed me most in the examination of the new compound (which in itself shows no remarkable crystallisable compounds), was its transformation into malic acid. It is known indeed, I mentioned the fact a moment ago, that Piria long since showed how to pass from asparagine and aspartic acid to malic acid, and I had assured myself by the most rigid proofs that this malic acid was identical with that from the mountain ash, from apples, from the grape, and from tobacco.

I therefore applied to the new acid the treatment discovered by Piria and actually transformed it into a new malic acid, very similar to the natural acid. It was so nearly allied to the latter that a chemist would have had difficulty in distinguishing them, even if he had been warned of their real disparity. Only, this malic acid had no action on polarised light, and the same was true of all its salts.

There are certain derivatives of these two malic acids which, on comparison, do not exhibit very clearly the real mutual dependence of the molecular arrangements of these curious isomers; but there are others in which it exhibits itself to its full extent. Let us consider, for example, the ordinary active bimalate of lime, and the corresponding inactive bimalate. Their chemical composition is exactly the same and their crystalline forms are alike, with the difference that the active one has four small hemihedral faces which are always absent in the inactive one. The result is that, when the active one is placed before a mirror, the image cannot be superposed on it, while the image of the inactive one is absolutely identical with and superposable on the reality which produces it. But in all that does not concern the hemihedral faces, the resemblance of the two forms is perfect.

Who could doubt, after that, the relation of the molecular arrangements in the two salts? Is it not evident that we have here to deal with a malic acid identical with the natural one, except for the simple suppression of its molecular asymmetry?

It is natural malic acid untwisted, if I may so express myself. The natural acid is a spiral stair as regards the arrangement of its atoms, this acid is the same stair made of the same steps, but straight in place of being spiral.

It might be asked whether the new acid is not the paratartaric member of the series, that is, the compound of the right malic acid with the left malic acid. That is improbable, for then not only would we have made an active body from an inactive one, we would have made two, a right and a left.

Besides, I have found that, just as there exists an inactive non-asymmetric malic acid, there is likewise an inactive non-asymmetric tartaric acid quite different from paratartaric acid, which cannot be resolved into a right tartaric acid and a left tartaric acid. It is impossible to doubt that we have here to do with right or left tartaric acid rendered non-asymmetric.

I have likewise discovered inactive amyl alcohol which gives rise to a whole series of inactive products corresponding to the series from active amyl alcohol.

We are now, thanks to the discovery of inactive substances, in possession of a fertile idea. A substance is asymmetric, right or left; by certain artifices of isomeric transformation, which must be sought and discovered for each particular case, it may lose its molecular asymmetry, become untwisted, to use a rough metaphor, and assume in the arrangement of its atoms a disposition with superposable image. In this way each asymmetric substance offers four varieties, or, better, four distinct sub-species: the right body, the left body, the combination of the right and the left, and the substance which is neither right nor left nor formed by the combination of the right and the left.

VII.

This general conclusion from the above-mentioned investigations throws a new light on our ideas of molecular mechanics. We discover that if the natural products elaborated under the influence of vegetable life are, as a rule, asymmetric, contrary to what we find in the case of artificial and mineral products, this disposition of the elementary particles is not a condition of the existence of the molecule,—that the twisted organic group can be untwisted, and so assume the ordinary character of artificial and mineral substances. Conversely, it seems to me logical to regard the latter as capable of exhibiting an asymmetric arrangement of their atoms after the manner of the natural products. The conditions for their production have still to be discovered.

To sum up what has been said, the groups of elementary atoms which constitute compound matter can assume two distinct states corresponding to the two general types under which every material object can be classified. The form of the group has either a superposable or a non-superposable image; but the latter type is double, for its inverse can exist equally well with itself. We must add the case of the association of these two inverse types, recalling the union by pairs of identical and non-superposable members in the higher animals. There are therefore in reality four remarkable arrangements for the groups of atoms which constitute matter. All our efforts should be bent to produce them for each particular species.

Almost all these conclusions are so rigorous that it is practically impossible to call them in question.

Thus, how can we refuse to admit that a right body has a possible left form, knowing as we do the significance of the right or left character? We might as well doubt that an irregular tetrahedron has its inverse, that a right helix has its left form, that a right hand has a possible left.

And consequently, if the mysterious influence to which the asymmetry of natural products is due should change its sense or direction, the constitutive elements of all living beings would assume the opposite asymmetry. Perhaps a new world would present itself to our view. Who could foresee the organisation of living things if cellulose, right as it is, became left; if the albumen of the blood, now left, became right? These are mysteries which furnish much work for the future, and demand henceforth the most serious consideration from science.

VIII.

Possibly, since chemistry has been up to the present time powerless to prepare asymmetric substances, one might fear that we should remain for ever in ignorance of a way of making the inverse forms of natural organic substances. Happily this fear is exaggerated. In fact I have discovered that ordinary chemical processes, such as the action of heat, enable us to pass from a right to a left substance, and *vice versa*. Thus, when right tartaric acid is heated under certain fixed conditions which it would take too long to specify here, it is transformed into left tartaric acid, or rather into paratartaric acid. And conversely under the same conditions precisely, left tartaric acid becomes right.

Here are ten or twelve grams of perfectly pure left tartaric acid, which have been obtained in this manner.

Their preparation has cost me much trouble. But M. BIOT was particularly anxious to study the dispersive properties of this left tartaric acid of such remarkable origin. He wished himself to defray the cost of the operation, which was very expensive, for the transformation depends on the employment of tartrate of cinchonine or of quinine, and the base is lost because the tartrate has to be heated to a temperature which destroys it. By this means I prepared paratartaric acid enough to yield twelve grams of left tartaric acid, which exhibited, in the inverse sense, absolutely the same optical characters as tartaric acid.

We must always consider every transformation like this of a natural asymmetric body into its inverse as a great advance of organic chemistry.

IX.

At the conclusion of our former meeting I referred to some observations to which it is now time that we devoted the attention which they deserve. These observations are connected with the comparison of the physical and chemical properties of the corresponding right and left isomers. I have already insisted on the perfect identity of all their properties, excepting always the inversion in their crystalline forms and the opposite sense of their optical deviations. The physical aspect, lustre of the crystals, solubility, specific weight, simple or double refraction, all these things are not merely alike, similar, nearly allied, but identical in the strictest sense of the word.

This identity is all the more remarkable since we shall see it replaced by a general and noteworthy contrast of the properties of the same substances when they are subjected to special conditions which I am about to indicate.

We have seen that all artificial or natural chemical compounds, whether mineral or organic, must be divided into two great classes: non-asymmetric compounds with superposable image and asymmetric compounds with non-superposable image.

Taking this into account, the identity of properties above described in the case of the two tartaric acids and their similar derivatives, exists constantly, with the unchangeable characters which I have referred to, whenever these substances are placed in contact with any compound of the class with superposable image, such as potash, soda, ammonia, lime, baryta, aniline, alcohol, ethers,—in a word, with any compounds whatever which are non-asymmetric, non-hemihedral in form, and without action on polarised light.

If, on the contrary, they are submitted to the action of products of the second class with non-superposable image,—asparagine, quinine, strychnine, brucine, albumen, sugar, etc., bodies asymmetric like themselves,—all is changed in an instant. The solubility is no longer the same. If combination takes place, the crystalline form, the specific weight, the quantity of water of crystallisation, the more or less easy destruction by heating, all differ as much as in the case of the most distantly related isomers.

Here, then, the molecular asymmetry of a substance obtrudes itself on chemistry as a powerful modifier of chemical affinities. Towards the two tartaric acids, quinine does not behave like potash, simply because it is asymmetric and potash is not. Molecular asymmetry exhibits itself henceforth as a property capable by itself, in virtue of its being asymmetry, of modifying chemical affinities. I do not believe that any discovery has yet made so great a step in the mechanical part of the problem of combination.

Let us try to illustrate the cause of these identities and differences. Let us imagine a right screw and a left screw separately penetrating two identical blocks of wood with the grain straight. All the mechanical conditions of the two systems will be the same. This will no longer be so from the moment that the same screws are associated with blocks which are themselves twisted in the same sense or in the opposite sense.

X.

Here is a very interesting application of the facts which have just been explained.

Seeing that the right and left tartaric acids formed such dissimilar compounds simply on account of the rotative power of the base, there was ground for hoping that, from this very dissimilarity, chemical forces might result, capable of balancing the mutual affinity of the two acids, and thereby supply a chemical means of separating the two constituents of paratartaric acid. I sought long in vain, but finally succeeded by the aid of two new bases, quinicine and cinchonicine, isomers of quinine and cinchonine, which I obtained very easily from the latter without the least loss.

I prepare the paratartrate of cinchonicine by neutralising the base and then adding as much of the acid as was necessary for the neutralisation, I allow the whole to crystallise, and the first crystallisations consist of perfectly pure left tartrate of cinchonicine. All the right tartrate remains in the mother liquor because it is more soluble. Finally this itself crystallises with an entirely different aspect, since it does not possess the same crystalline form as the left* salt. We might almost believe that we were dealing with the crystallisation of two distinct salts of unequal solubility.

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* [" Right" in original.]

XI.

But the difference in properties of corresponding right and left substances when they are subjected to asymmetric forces, seems to me to be interesting in the highest degree on account of the ideas which it suggests to us in regard to the mysterious cause which presides over the asymmetric arrangement of the atoms in natural organic substances. Why this asymmetry? Why the one asymmetry rather than its inverse?

Carry yourselves back with me in thought to the time when, having recognised the absolute identity of the chemical and physical properties of the corresponding right and left substances, I had not any idea, not even the suspicion, of possible differences between these substances. It was, in fact, after an interval of several years that I recognised these similarities and differences.

It was then impossible for me to understand how nature could make a right substance without at the same time making the left substance. For the same forces which are at work at the moment at which the molecule of right tartaric acid is elaborated, must, it seemed, yield a left molecule also, and there would have been nothing but *paratartaric* compounds.

Why even right or left substances at all? Why not simply non-asymmetric substances; substances of the order of inorganic nature?

There are evidently causes for these curious manifestations of the play of molecular forces. To indicate them in a precise manner would certainly be a difficult matter. But I believe that I am not deceived when I say that we know one of their essential characters. Is it not necessary and sufficient to admit that at the moment of the elaboration of the primary principles in the vegetable organism, an asymmetric force is present? For we have just seen that there is only a single case in which the right molecules differ from the left, the case where they are submitted to influences of an asymmetric character.

Do these asymmetric actions, possibly placed under cosmic influences, reside in light, in electricity, in magnetism, or in heat? Can they be related to the motion of the earth, or to the electric currents by which physicists explain the terrestrial magnetic poles? It is not even possible at the present time to express the slightest conjecture in this direction.

But I regard as necessary the conclusion that asymmetric forces exist at the moment of the elaboration of natural organic products; forces which would be absent, or ineffectual, in the reactions of our laboratories either on account of the violent course of these phenomena, or because of some other unknown circumstance.

XII.

We now reach a final experiment which does not yield in interest to any of those which precede, in respect to the manifest proof which it will give us of the influence of asymmetry in the phenomena of life. We have just seen asymmetry intervening to modify chemical affinities; but the reactions involved were purely inorganic, artificial, and we know all the prudence that must be observed in the application of the results of the laboratory to the phenomena of life. On this account I kept to myself almost all the views expressed in this Lecture till the moment that I recognised in the most certain manner that molecular asymmetry exhibited itself as a modifier, no longer of the reactions of inorganic nature, but of those of physiological character, in fermentations.

Here is the remarkable phenomenon to which I refer.

It had long been known, from the observation of a

German manufacturer of chemical products, that the impure tartrate of lime of the works, mixed with organic matters, when left under water in summer, could ferment, giving various products.

Knowing this, I set the ordinary right tartrate of ammonia to ferment in the following manner. I took the very pure crystallised salt, dissolved it, adding to the liquor a clear solution of albumenoid matter. One gram of dry albumenoid matter was sufficient for one hundred grams of tartrate. Very often it happens that the liquid ferments spontaneously when placed in an oven. I say very often; but it may be added that this will always take place if we take care to mix with the liquid a very small quantity of one of those liquids with which we have succeeded in obtaining spontaneous fermentation.

So far there is nothing peculiar; it is a tartrate fermenting. The fact is well known.

But let us apply this method of fermentation to paratartrate of ammonia, and under the above conditions it ferments. The same yeast is deposited. Everything shows that things are proceeding absolutely as in the case of the right tartrate. Yet if we follow the course of the operation with the help of the polarising apparatus, we soon discover profound differences between the two operations. The originally inactive liquid possesses a sensible rotative power to the left, which increases little by little and reaches a maximum. At this point the fermentation is suspended. There is no longer a trace of the right acid in the liquid. When it is evaporated and mixed with an equal volume of alcohol it gives immediately a beautiful crystallisation of left tartrate of ammonia.

Let us note, in the first place, two distinct things in this phenomenon. As in all fermentation properly so called, there is a substance which is changed chemically, and correlatively there is a development of a body possessing the aspect of a mycodermic growth. On the other hand, and it is this which it is important to note, the yeast which causes the right salt to ferment leaves the left salt untouched, in spite of the absolute identity in physical and chemical properties of the right and left tartrates of ammonia as long as they are not subjected to asymmetric action.

Here, then, the molecular asymmetry proper to organic substances intervenes in a phenomenon of a physiological kind, and it intervenes in the rôle of a modifier of chemical affinity. It is not at all doubtful that it is the kind of asymmetry proper to the molecular arrangement of left tartaric acid which is the sole and exclusive cause of the difference from the right acid, which it presents in relation to fermentation.

Thus we find introduced into physiological principles and investigations the idea of the influence of the molecular asymmetry of natural organic products, of this great character which establishes perhaps the only well marked line of demarcation that can at present be drawn between the chemistry of dead matter and the chemistry of living matter.

XIII.

Such, gentlemen, are in co-ordinated form the investigations which I have been asked to present to you.

You have understood, as we proceeded, why I entitled my exposition, " On the Molecular Asymmetry of Natural Organic Products." It is, in fact, the theory of molecular asymmetry that we have just established, one of the most exalted chapters of the science. It was completely unforeseen, and opens to physiology new horizons, distant, but sure.

I hold this opinion of the results of my own work without allowing any of the vanity of the discoverer to mingle in the expression of my thought. May it please God that personal matters may never be possible at this desk. These are like pages in the history of chemistry which we write successively with that feeling of dignity which the true love of science always inspires.

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THE
ELECTROLYSIS
OF
ORGANIC COMPOUNDS

PAPERS BY

HERMANN KOLBE

(1845-1868)

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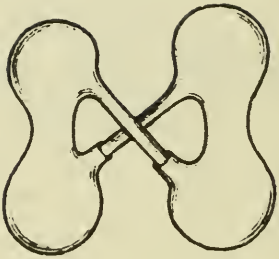

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PREFACE.

THE decomposition of organic compounds by electrolysis is a subject that has engaged the attention of chemists for more than half a century. The investigation of the subject has enabled the synthesis of a variety of important and interesting substances to be effected; and, in the hands of Kolbe especially, it was also of great service in the development of certain theoretical views concerning organic compounds. The present reprint contains Kolbe's account of his earliest experiments which have any bearing on the matter, as well as his classical memoir upon the electrolysis of valerianates and acetates, and it thus furnishes the first chapters in the history of this line of investigation. Readers who are unfamiliar with the formulæ generally employed by Kolbe will find it useful to recollect that the atomic weights of carbon, oxygen, and sulphur are, with him, 6, 8, and 16 respectively. The "barred" formulæ (made use of in one of the papers only) coincide exactly with those employed later without bars.

A few obvious misprints in the originals have been corrected.

L. D.

THE ELECTROLYSIS OF ORGANIC COMPOUNDS.

EARLY EXPERIMENTS.

WHAT would appear to be the earliest references by Kolbe to the effects of electrolysis upon solutions of organic substances, are found in his paper, "Contributions to the Knowledge of Conjugated Compounds," printed in the *Annalen der Chemie und Pharmacie*, Vol. 54 (1845), pp. 145-188. At the time at which this paper appeared, it seems as if Kolbe only regarded the application of electrolysis to such solutions as a means of submitting the dissolved substances to the reducing influence of hydrogen at the moment of its liberation. The following references are made in the paper to the reducing effects of the galvanic current:—

At pp. 155-156, where he states the effects of various reducing agents upon sulphite of perchloride of carbon, $\mathrm{C\,Ɵl_2SO_2}$ (Trichlormethyl-sulphonyl chloride), in converting it into a substance which he calls sulphite of chloride of carbon, and to which he assigns the formula $\mathrm{C\,Ɵl\,SO_2}$, he says:—

"Hydrogen brings about the same reduction when it comes into contact, in the nascent state, with dissolved sulphite of perchloride of carbon; for example, when iron or zinc is digested with an acidulated solution of that compound in highly diluted alcohol; or when the same liquid is decomposed by the galvanic current.*

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* In order to guard against the compound being oxidized by the oxygen separated at the anode, the anode must be an easily oxidized metal. I employed amalgamated zinc plates.

The hydrogen set free in the process always has a peculiar unpleasant smell."

At pp. 168-169, in the section on chlor-elayl hyposulphuric acid, $\cancel{H}O + C_2\cancel{H}_2\cancel{Cl}S_2O_5$ (Chlormethyl-sulphonic acid), he says :—

"Metallic zinc dissolves in chlor-formyl hyposulphuric acid * with the evolution of hydrogen and the formation of chloride of zinc; the product is a mixture of the zinc salts of chlor-formyl hyposulphuric and chlor-elayl hyposulphuric acids. The separation of the second equivalent of chlorine from the chlor-formyl hyposulphuric acid clearly takes place, therefore, with greater difficulty than the elimination of the first equivalent. In that decomposition there is always a small part only of the chlor-formyl hyposulphuric acid converted into the compound richer in hydrogen. More of it is obtained when the evolution of hydrogen is maintained for a longer time by the addition of another acid—sulphuric acid, for example; but even in this way the last portions of the chlor-formyl hyposulphuric acid cannot be entirely removed. This succeeds only by the decomposition of the acidulated solution of a salt of chlor-formyl hyposulphuric acid or of sesquichloro-carbohyposulphuric acid † by means of the galvanic current. I proceeded according to the following method:

About 50 grms. of sesquichloro-carbohyposulphate of potash were dissolved in water, mixed with sulphuric acid, and digested with zinc until the liquid was quite saturated with zinc salts. The solution of the metal takes place with brisk evolution of hydrogen gas, which diffuses abroad, during the process, a peculiar disagreeable smell possessing some similarity to that of sulphuret

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* [$\cancel{H}O + C_2\cancel{H}\cancel{Cl}_2S_2O_5$ (Dichlormethyl-sulphonic acid).]

† [$\cancel{H}O + C_2\cancel{Cl}_3S_2O_5$ (Trichlormethyl-sulphonic acid).]

of carbon. The greater part of the zinc crystallises out as sulphate of zinc and potash when the hot concentrated solution cools. The liquid poured off from this is precipitated, boiling, with carbonate of potash, filtered, and evaporated to dryness, and the powdered residue is extracted with boiling alcohol of 80°. The dry saline mass which remains behind after the evaporation of the alcohol consists of a mixture of chlor-formyl and chlor-elayl hyposulphates of potash. The quantity of the latter is further increased by another similar treatment with zinc and sulphuric acid. I then dissolved the residue, which only contained a little chlor-formyl hyposulphuric acid, in water again, made it slightly acid with sulphuric acid, and submitted it, in a suitable vessel, to the decomposing action of the galvanic current generated by two cells of the Bunsen zinc-carbon battery. The electrodes were two amalgamated zinc plates.

The operation is interrupted when the evolution of hydrogen gas, which is brisk at first, ceases, and metallic zinc is deposited upon the anode. The dissolved zinc salts are precipitated by means of carbonate of potash, and the filtered and acidulated solution is again decomposed by the current; and this is repeated about three or four times, or until all has been converted into chlor-elayl hyposulphuric acid."

At pp. 174-176, in describing the preparation of methyl hyposulphuric acid, $ĦO + C_2Ħ_3S_2O_5$ (Methyl sulphonic acid), he says :—

"I employed sesquichloro-carbohyposulphate of potash for its preparation.

70 grms. are dissolved in three times this quantity of water, and the *neutral* liquid is decomposed, in the same manner that I stated under chlor-elayl hyposulphuric acid, by the galvanic current from two cells of a Bunsen zinc-carbon battery. Two amalgamated zinc plates served

as electrodes. The decomposition proceeds quietly and without evolution of gas at first, with a somewhat considerable elevation of temperature. Only after a large part of the sesquichloro-carbohyposulphuric acid is converted into methyl hyposulphuric acid does hydrogen become free at the cathode. This circumstance can be made use of in order to determine at any time, approximately at least, how much chlorine has been exchanged for hydrogen.

According to the formula:

$$\left.\begin{array}{r} \mathrm{KO} + \mathrm{C_2\text{Ɵ}l_3S_2O_5} \\ \mathrm{6Zn} \\ \mathrm{6\text{Ħ}O} \end{array}\right\} = \left\{\begin{array}{l} \mathrm{KO} + \mathrm{C_2\text{Ħ}_3S_2O_5} \\ \mathrm{6ZnO} \\ \mathrm{3\text{Ħ}\text{Ɵ}l} \end{array}\right.$$

it is calculated that 57 grms. of zinc are necessary for the conversion of 70 grms. of sesquichloro-carbohyposulphate of potash. The deflection of the magnetic needle of a Weber's tangent galvanometer introduced into the circuit, amounted in these experiments, on the average, to between 50° and 60°, which corresponds, in the case of the instrument employed, to an average strength of current of about 82. Since with this strength of current, about 10 grms. of zinc are dissolved in an hour, the above decomposition would be finished in 6 hours.

After the action of the current for one hour, the liquid was so saturated with chloride of zinc that metallic zinc was deposited upon the cathode in large quantity. It was therefore precipitated, boiling, with carbonate of potash; the filtered alkaline solution was evaporated to the original volume and exposed anew to the action of the current for an hour, until the quantity of the separated carbonate of zinc had increased so greatly that reduction upon the cathode ensued.

It was only after 45 grms. of zinc, from the anode, were dissolved, in the course of repeated operations, that a disengagement of hydrogen commenced at the other pole. The dissolved salts were now chlor-elayl hyposulphate and methyl hyposulphate of potash, mixed with a large excess of the chloride of potassium produced. In order to separate the latter as much as possible, I evaporated the solution to dryness and treated the residue with boiling alcohol of 80°. After the alcohol was distilled off, the soluble salts were again mixed with water and, after the addition of a little carbonate of potash, again decomposed by the current until 40 grms. of zinc were dissolved afresh. The evolution of hydrogen was very brisk at the end.

After the decomposition had continued altogether for 10 hours, I felt sure that the chlor-elayl hyposulphuric acid was completely converted into methyl hyposulphuric acid.

It is a remarkable phenomenon that in the decomposition of an *acid* solution of sesquichloro-carbohyposulphate of potash by means of the galvanic current, the exchange of the chlorine for hydrogen is at an end with the formation of chlor-elayl hyposulphuric acid, whereas, in presence of free alkali it extends to the third equivalent of chlorine also; for I have never obtained a trace of methyl hyposulphuric acid in the first case. It is difficult to explain to one's self why the hydrogen exerts towards chlorine, as soon as the acid to be decomposed is united to a base, a greater attraction than it does when the acid is presented to it in the free state."

OBSERVATIONS ON THE OXIDIZING POWER OF OXYGEN WHEN DISENGAGED BY MEANS OF VOLTAIC ELECTRICITY.*

IN describing in a former paper † the properties of sesquichloro carbohyposulphuric acid, I stated that this body resists the action of the most powerful oxidizing agents, such as chromic acid, nitric acid, and even nitrohydrochloric acid. I likewise stated the change it undergoes by the action of a voltaic current, when an easily oxidizable metal is used for the positive pole. By this means another copulated acid is produced, in which one or more equivalents of chlorine are replaced by corresponding proportions of hydrogen.

I have since observed that this acid is completely decomposed on employing two platina plates as electrodes; by which arrangement oxygen is disengaged at the positive pole. The following details, which contain a more perfect account of this observation, I hope will be acceptable to the Society.

On decomposing a concentrated solution of sesquichloro-carbohyposulphate of potash by a strong voltaic current (obtained by four elements of Bunsen's battery), at the commencement no hydrogen can be observed at the negative pole in consequence of the formation of the above-mentioned copulated acids, whilst chlorine, carbonic acid, and afterwards oxygen, are evolved at the positive pole. At the moment decomposition commences a distinct acid reaction of the solution is perceptible, owing to the formation of free hydrochloric and sulphuric acids; in a later stage of the process, these acids increasing in quantity, hydrogen appears at the negative pole, until finally, after all the hydrochloric acid has been decomposed, and the disengagement of chlorine has ceased, small octahedral crystals of perchlorate of potash are deposited from the solution, which now contains a large amount of free sulphuric acid and bisulphate of potash. The formation however of perchloric acid in this process is always preceded by that of chloric acid; for on evaporating the solution in an earlier stage of the decomposition, beside the before-mentioned octahedral crystals, the well-known rhombic plates of chlorate of potash are obtained.

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* [From Memoirs and Proceedings of the Chemical Society of London. Vol. 3 (1848), pp. 285-287. Read December 7, 1846.]

† Liebig's *Annalen der Chemie*, liv. pp. 156, 160.

The following formula represents the most probable decomposition sesquichloro-carbohyposulphuric acid undergoes by the action of a voltaic current:—

$$\begin{array}{r} KO + C_2\,Cl_3\,S_2\,O_5 \\ 12O \end{array} \left\{ \begin{array}{l} KO + ClO_7 \\ 2SO_3 \\ 2CO_2 \\ 2Cl. \end{array} \right.$$

The production of perchloric acid in an acid solution is certainly a fact worthy of attention, for according to all the observations hitherto made, combination between chlorine and oxygen could only be effected in presence of a free alkaline basis ready to unite with the newly formed acid; but ascertained as it is by a great number of careful experiments, it is another proof of the unparalleled negative power of oxygen when evolved by means of voltaic action.

These observations induced me to make the following experiments.

A neutral solution of chloride of potassium was decomposed in the same manner by a strong voltaic current;

it immediately became alkaline, whilst hydrogen and chlorine were disengaged. The formation of chlorate of potash, which took place under these circumstances, can evidently be considered only as the result of the ordinary chemical action of chlorine upon caustic potash. On mixing however a solution of chloride of potassium with sufficient sulphuric acid to set free all the muriatic acid, and passing the voltaic current through it as before, chlorate of potash was nevertheless formed, which was subsequently converted into perchlorate of potash.

The transformation of oxy-acids of chlorine, such as liquid hypochloric acid (ClO_4), or of a solution of chlorate of potash, into perchloric acid by means of voltaic action, has been mentioned by Berzelius. I have ascertained, moreover, that when a voltaic current is passed through hydrochloric acid, especially when previously mixed with some sulphuric acid, free chloric and perchloric acids are formed, after the disengagement of a considerable quantity of chlorine.

A concentrated solution of chloride of ammonium evolves hydrogen at the negative pole but neither oxygen nor chlorine at the positive pole. But the surface of the platina plate representing the latter pole is covered with small yellowish oily drops of chloride of nitrogen, which as soon as the two poles are brought into contact decomposes with a more or less violent explosion, chlorine and nitrogen being evolved. This experiment illustrates at once the formation of this compound and its highly explosive character.

Cyanide of potassium if dissolved in water is easily oxidized by a voltaic current, and converted into cyanate of potash, but I did not succeed in obtaining a percyanate of potash. I was not more successful in endeavouring to form a fluorate of potash from the fluoride of potassium by the same means.

I have not prosecuted my experiments further upon inorganic substances, having from some observations on the behaviour of organic compounds under the action of the voltaic current obtained results of so much greater interest, as to induce me to give them my exclusive attention; and at a future time, when I have completed the investigation, I shall beg leave to communicate it to the Chemical Society.

ON THE DECOMPOSITION OF VALERIANIC ACID BY THE VOLTAIC CURRENT.*

THE very remarkable changes which a series of organic compounds undergoes by means of the voltaic current, have induced me to make that mode of decomposition the subject of a thorough investigation. As however the numerous difficulties which present themselves in researches of this nature, and the immense extent of the field which opens before us, do not admit of the results being communicated in a complete and connected form, I beg to lay before the Chemical Society a short preliminary notice of the changes which valerianic acid undergoes when exposed to the oxidizing action of the voltaic current, reserving a more complete description of the products obtained till the investigation shall have been brought to a close.

When the voltaic current, excited by six pairs of Bunsen's carbo-zinc battery, is permitted to act on a concentrated neutral solution of valerianate of potash in the cold, two plates of platinum forming the electrodes, a brisk evolution of gas takes place simultaneously from both; the gases evolved consist of hydrogen, carbonic acid and a new carbo-hydrogen, but contain no traces of oxygen gas as long as the solution of valerianate of potash does not become too much exhausted. At the same time a light oily liquid separates at the surface, having an agreeable æthereal odour, and the alkaline solution ultimately consists chiefly of carbonate and bicarbonate of potash, the latter of which generally separates during the operation in a crystalline form.

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* [From Memoirs and Proceedings of the Chemical Society of London, Vol. 3 (1848), pp. 378-380. Read April 19, 1847.]

The neutral æthereal oil is a mixture of two compounds; the one containing oxygen, the other perfectly free from it. By the action of an alcoholic solution of potash the former is decomposed, and the latter can then, by means of water, be separated unchanged. In the pure state it exists in the form of a light colourless æthereal oil, possessing an agreeable aromatic smell. It is insoluble in water, but soluble in alcohol and æther; it boils at 108° C. without decomposition, and has the composition $C_8 H_9$. Oxygen and iodine are without action upon it, but chlorine, bromine, and fuming nitric acid form with it products of substitution.

The oil containing oxygen, which in the first instance was found mixed with this substance, I have not yet been able to obtain in a pure state; but several circumstances render it more than probable that it is formed by the union of valerianic acid with the oxide of the above carbo-hydrogen. An alcoholic solution of potash treated with it is found to contain as a product of decomposition a considerable amount of valerianate of potash. But on account of the small quantity of material which has been at my disposal, I have not succeeded in separating the alcohol $C_8 H_{10} O_2$, which must have been formed at the same time.

The gaseous carbo-hydrogen, which is evolved with the hydrogen, is a substance analogous to olefiant gas; it is characterized by a peculiar æthereal smell, and has a specific gravity double that of olefiant gas. It unites with chlorine even in the dark, forming a heavy oily liquid, having a marked similarity to chlorelayl, and is generally composed of a mixture of several products of substitution. Its rational composition is expressed by the formula $C_8 H_8$. The changes which valerianic acid undergoes, in accordance with the foregoing experiments, are capable of a very simple explanation, if we consider that acid as a conjugated combination of the carburetted hydrogen, or the radical $C_8 H_9$ with oxalic acid, in a similar manner to the new view taken of the constitution of acetic acid. For whilst by the addition of one atom of oxygen oxalic acid becomes converted into carbonic acid, this radical is set free; but a portion of it unites with the excess of oxygen to form an oxide, and this enters into combination with a portion of undecomposed valerianic acid, giving rise to a new æther, $C_8 H_9 O + C_8 H_9 C_2 O_3$.

Another portion of the radical is probably decomposed at the moment of its formation, in consequence of the concomitant evolution of heat into hydrogen and the gaseous carbohydrogen $C_8 H_8$. This latter view is supported by the fact, that if the temperature of the solution of valerianate of potash exceeds a certain point during the decomposition, not a single drop more of the ætherial oil is produced.

The following formula will throw light on this decomposition: —

$$\left.\begin{matrix}KO + C_8 H_9 C_2 O_3 \\ O\end{matrix}\right\} = \left\{\begin{matrix}KO + 2CO_2 \\ C_8 H_9.\end{matrix}\right.$$

Both butyric and acetic acids are acted on in a similar manner to valerianic acid ; the products of decomposition of acetic acid are all gaseous, and appear to contain oxide of methyl. Butyric acid gives in addition to the gaseous compounds a volatile oil composed of $C_6 H_7$.

The minute description of this product will form the subject of a future memoir.

The foregoing investigation has been carried out during the late session in the laboratory of Dr Lyon Playfair, as whose assistant I have been engaged during that time ; and I cannot allow this opportunity to pass by without thanking him for the kindness and liberality which he has shown in placing his laboratory at my disposal, in leaving so much of my time on my own hands, and in rendering me every assistance in his power.

RESEARCHES ON THE ELECTROLYSIS OF ORGANIC COMPOUNDS.*

THE following investigation has chiefly arisen from some former observations† respecting the transformations of chloro-carbo-hyposulphuric acid, hydrochloric acid, and several other substances under the influence of oxygen, when liberated in the circuit of the galvanic current.‡ The facility with which, particularly the former acid, resisting in the moist way the most powerful oxidizing processes, is decomposed under these circumstances, appears to point to electrolysed oxygen as one of the most valuable oxidizing agents which are at the disposal of the chemist. Its application in chemical decompositions acquires additional importance, since its intensity may be varied, either by concentrating and heating the liquid, or by increasing or diminishing the number of elements producing the electrical current.

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* [From The Quarterly Journal of the Chemical Society of London, Vol. 2 (1850), pp. 157-184.]

† Observations on the oxydizing action of oxygen when disengaged by means of voltaic electricity in the "Memoirs and Proceedings of the Chemical Society," vol. III. p. 285.

‡ In the above cited investigation it was intended to state, that in the oxidation of hydrochloric acid by means of the electrical current, chloric acid appears at the positive pole even without the presence of an alkali. The sense of the sentence has been seriously altered by a misprint on page 287, line 8 from the top, *hypochloric* having been substituted for "hydrochloric acid." The sentence should have been as follows: "I have ascertained that when a voltaic current is passed through hydrochloric acid, especially when previously mixed with some sulphuric acid, free chloric and perchloric acids are formed after the disengagement of a considerable quantity of chlorine."

Starting from the hypothesis that acetic acid is a conjugated compound of oxalic acid and the conjunct methyl, I considered it, under these circumstances, not at all improbable that electrolysis might effect a separation of its conjugated constituents, and that, in consequence of a simultaneous decomposition of water, carbonic acid, as a product of the oxidation of oxalic acid, might appear at the positive, while methyl, in combination with hydrogen, viz., as marsh-gas, would be observed at the negative pole.

The decomposition, which actually takes place, is not in perfect accordance with this supposition, as will be seen by the experiments hereafter described. The results obtained, however, are by no means less interesting, and deserve particular attention, opening as they do a prospect that the electrolytical decomposition of organic compounds will afford most important disclosures with reference to their chemical constitution.

After having made some preliminary experiments with several acids belonging to the acetic acid series, the products of the oxidation of valerianic acid appeared particularly suited for minutely following out the course of this decomposition. I therefore consider it convenient, first to describe the phenomena attending the decomposition of this acid, inasmuch as they form the basis for further experiments.

ELECTROLYSIS OF VALERIANIC ACID.

Valerianic acid being, like acetic acid, a bad conductor of electricity, I employed in the electrolytical decomposition a concentrated solution of its potash salt, prepared by neutralizing carbonate of potash, free from chloride, with pure valerianic acid, distilling at 175° (347° F.)*

The decomposing apparatus, *Fig.* 1,† is a glass cylinder, 11 inches in height and 2½ inches in diameter, which may be closed by means of a cork; in this is fastened a cylinder of sheet copper, closely approaching the sides of the glass, and to which is soldered the copper wire *a*, slightly projecting from the vessel. Within the copper sheet is another cylinder of platinum foil of somewhat smaller diameter, terminating in the platinum wire *b*, and prevented contact with the copper by a narrow ring of glass, placed between the two cylinders at their lower extremities. Both wires, as well as the large delivery tube *c*, are cemented perfectly air tight into the cork, the tube being of sufficient diameter to admit of emptying and filling the cylinder without inconvenience.

On passing the electrical current, produced by four elements of Bunsen's zinco-carbon battery, through the apparatus filled to the height *c c*, with a concentrated solution of valerianate of potash, the platinum wire *b* forming the positive pole, the negative wire being in connexion with the cylinder of copper, the following phenomena are observed: A lively evolution of gas takes place simultaneously with the formation of yellowish oily drops, possessing an agreeable etherial odour; on agita-

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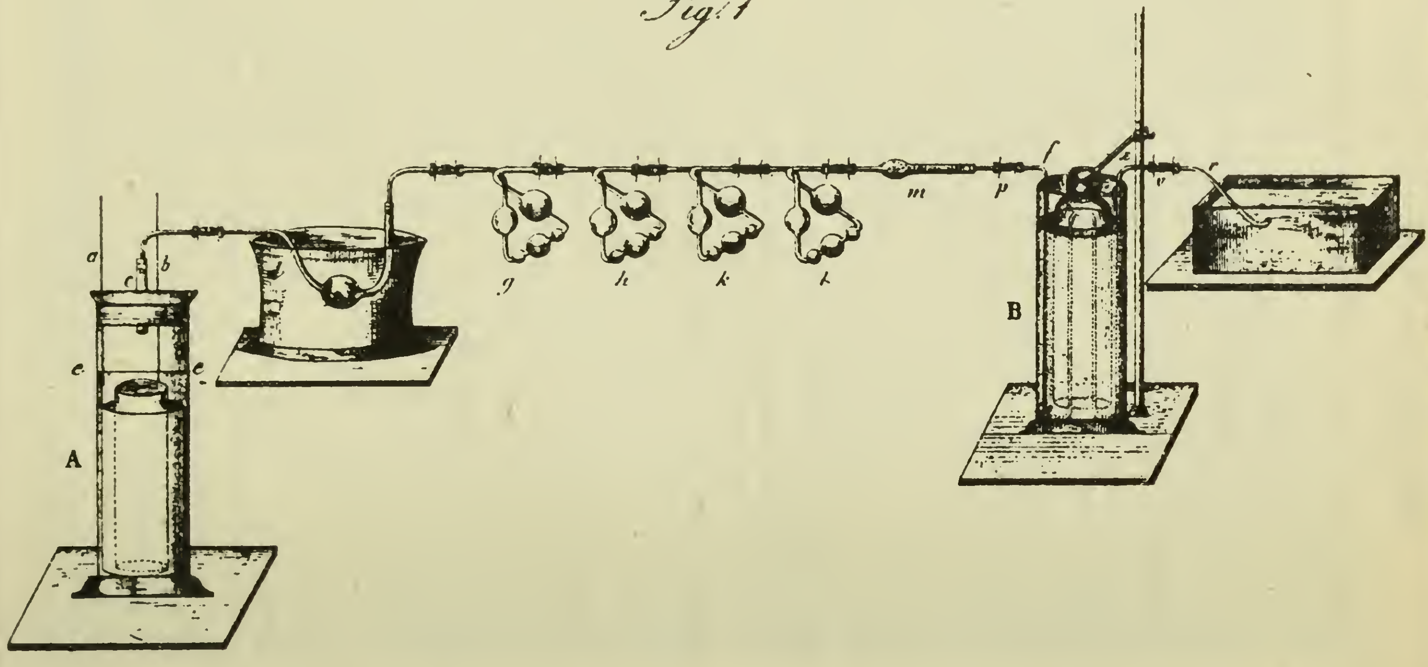
* The presence of chloride of potassium gives rise to the formation of secondary chlorinated products requiring more minute investigation. The soda salt cannot be employed with advantage, inasmuch as the bicarbonate, which is formed during the decomposition, enfeebles to a great extent the electrical current, interrupting it entirely towards the end of the process. The bicarbonate of potash being more soluble, a few crystals only separate during the decomposition.

† [The accompanying figure illustrates Kolbe's paper in *Liebig's Annalen*, Vol. 69. It was more suitable for reproduction than the one in the Chemical Society's Journal.]

Annalen der Chemie u. Pharm. LXIX. 3. Heft. (1849.) [illegible]

Fig: 1



tion with the liquid, the oil remains undissolved, even on the addition of potash.

The remarkably odorous gases which are evolved during the process, contain, after complete expulsion of air from the apparatus, no longer a trace of oxygen, and may be ignited without fear of explosion. Carbonic acid and hydrogen, however, are present in considerable quantities, in conjunction with a third gas burning with a highly luminous flame, and imparting to the mixture its peculiar odour.

After the action of the current had been continued for several hours, the stratum of oily liquid on the surface had increased to the height of several lines, while the valerianate of potash was almost completely converted into a mixture of carbonate and bicarbonate of potash, the latter generally crystallizing towards the end of the operation.

With a view of ascertaining at which pole each of these products was liberated, I endeavoured to separate the electrodes by means of a porous diaphragm, which allowed me to collect separately the substances disengaged at either pole. I employed for this purpose a porous cell of clay, into which a small glass tube of nearly equal diameter, and open at both ends, was fastened air tight by means of a caoutchouc joint. This arrangement containing the platinum foil, forming the positive pole, and admitting of being closed by a cork furnished with a delivery tube, was introduced into the copper cylinder of the decomposing apparatus.

Both cylinders were now filled with a solution of the neutral valerianate to the height of about one inch above the caoutchouc joint. It was found that on closing the circuit, only hydrogen and free potash were disengaged at the copper pole, while all the other products, the etherial oil, carbonic acid, the odorous gas, and the free acid, (which, in this arrangement, prevented the formation of a carbonate,) appeared at the positive pole.

VALYL.

In the experiments instituted for the preparation* of the etherial oil, I preferred removing the product from time to time with a pipette, which I introduced through the open glass tube *c*, the process being continued until the solution was entirely exhausted of valerianic acid.

The alkaline residue was now again introduced into a porcelain dish, and neutralized with pure valerianic acid; the neutral solution being again repeatedly subjected to the process of electrolysis, until a sufficient quantity of oil had been collected.

The impure product, after repeated agitation with water, exhibits the following properties: It is miscible with alcohol and ether in all proportions, insoluble in water, and of lower specific gravity than that liquid. It possesses an agreeable etherial odour. Chloride of calcium is dissolved by it, particularly in the cold, and hence the slight turbidity which is observed when the clear anhydrous liquid is subjected to ebullition. It commenced boiling a few degrees above 100° (212° F.), the temperature rapidly rising to 160° (320° F.) and even higher; the last products possess a penetrating disagreeable odour, and differ in a remarkable manner from the liquid which passed over at a lower temperature. The quantity of carbon found in the distillate, collected at different temperatures, diminishes with the rise of the boiling point, decreasing from 80 to 76 per cent., while the amount of oxygen, varying between 6 and 10 per cent., is found in the inverse proportion. The disagreeably smelling oil distilling towards the end of the operation, appears to be formed only by the action of chloride of calcium on the original compound; but even when distilled in vacuo at very low temperatures, the distillates collected at different stages of the process exhibit a composition not less variable.

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* The decomposing apparatus employed in this and the following experiments, was placed in a vessel of water at the temperature of 0° C. The solution of valerianate of potash being moderately heated, hardly a trace of the oil is produced, the decomposition taking place in an entirely different manner.

It appears that the impure oil is a mixture of at least two substances, its deportment with an alcoholic solution of potash affording a powerful argument in favour of this opinion.

On boiling a mixture of this oil with an alcoholic solution of potash in a flask connected with the lower extremity of a Liebig's condenser, placed in such a position as continually to return the condensed products to the boiling fluid, the following phenomena are observed. Immediately on the application of heat, bubbles of a gaseous body are seen to rise, possessing the characteristic odour of the compound, which, in the electrolytical decomposition of valerianate of potash, accompanies the evolution of hydrogen and carbonic acid: hence, it appears that this gas, which is held in solution by the liquid, becomes liberated when heat is applied. In a short time the evolution ceases, and the odour of the gas is no longer perceptible; when in a full state of ebullition the oil, previously colourless, assumes a yellowish tint, and becomes slightly turbid, while a heavy, apparently oily liquid collects at the bottom of the flask, which on examination is found to be an aqueous solution of valerianate of potash. To effect complete decomposition of the constituent affected by potash, at least half an hour's ebullition is necessary.

On mixing the liquid after boiling, with a large excess of water, a light etherial oil separates, which, after standing for some time, collects on the surface into a clear transparent layer; repeatedly washed with fresh portions of water, and subsequently dried by chloride of calcium, it exhibits a pretty constant boiling point at 108° (226.4 F.). The fraction distilling at this temperature, when subjected to a second rectification boiled at the same point, the first three-fourths of the product being collected. The quantity of pure substance thus obtained exceeds half the original volume of the impure oil. The purified compound presents itself in the form of a clear pellucid fluid of agreeable odour, and first insipid, though afterwards of a burning taste; miscible with alcohol and ether in all proportions, it is perfectly insoluble in water, which readily precipitates it from its alcoholic and etherial solutions. It boils exactly at 108° (226.4° F.), distilling without change to the last drop. It is inflammable, and burns with a strongly luminous smoky flame. It dissolves chloride of calcium, but to a less extent than the impure oil. Its specific gravity at 18° (64.4 F.) is 0.894, that of the vapour being 4.053.

By combustion with oxide of copper * the following results were obtained:

I. 0.1825 grm. of substance gave
0.5630 ,, ,, carbonic acid, and
0.2610 ,, ,, water.

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* It is impossible to burn this substance, so rich in carbon, with either protoxide of copper or chromate of lead alone, a small quantity of metallic carbide being formed, which occasions a deficiency in the carbon amounting to between 0.5 and 0.8 per cent.; hence combustion with oxygen is absolutely necessary, the latter being conveniently evolved from small pieces of perchlorate of potash placed at the posterior end of the combustion tube, a plug of dry asbestos preventing contact with the protoxide of copper. In addition to this precaution, it is necessary to attach to the common bulbs a tube containing solid potash, in order to absorb the aqueous vapour volatilized in the gases passing through the potash apparatus.

II. 0.1578 grm. of substance gave
0.4855 ,, ,, carbonic acid, and
0.2260 ,, ,, water.

These numbers lead to the formula

$C_8 H_9$

	Theory.		Experiment.	
8 equiv. of Carbon .	600.0	84.2	84.1	84.0
9 ,, ,, Hydrogen .	112.5	15.8	15.9	15.8
	712.5	100.0	100.0	99.8

This compound possesses the composition of the, hitherto hypothetical, radical of the still unknown alcohol belonging to butyric acid (C_8H_9O,HO), or the radical which, in valerianic acid, we assume to be in combination with oxalic acid. I propose to call it valyl.

Without entering here minutely into the question, whether valyl is indeed the radical of an alcohol corresponding to methyl, ethyl, and amyl; I will only mention one fact, which, in support of such a supposition, may seem of some importance; viz. that the specific gravity of its vapour exactly coincides with the number indicated by theory. According to the analogy of the methyl and ethyl series this compound would contain 4 vol. of carbon vapour, and 9 vol. of hydrogen condensed into 1 vol., hence the density of its vapour would be 3.9387, viz.:

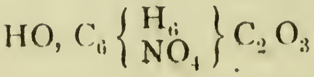
4 vol. of Carbon	3.3168
9 ,, ,, Hydrogen . . .	0.6219
1 vol. of Valyl	3.9387

Experiment gave the following results:

Substance employed . . .	0.2085 grm.
Volume of vapour observed . .	63.3cc
Temperature	133.3° C.
Barometer	752.9^{mm}
Mercury-column	64.0^{mm}
Pressing oil-column at 17° C .	262.0^{mm}

The specific gravity of valyl vapour as calculated from the foregoing numbers is 4.053, closely coinciding with the theoretical value.

Valyl is difficultly acted on by oxidizing agents; moderately strong nitric acid, or a mixture of chromate of potash and sulphuric acid have very little action upon it even after continuous ebullition; strong fuming nitric acid, however, especially after the addition of sulphuric acid, completely oxidizes this compound, nitrous fumes being evolved, while the oil gradually disappears. On neutralizing with carbonate of baryta, evaporating the filtrate to dryness, and extracting the residue with strong boiling alcohol the nitrate of baryta remains undissolved. The alcoholic liquid when evaporated leaves a saline residue, the distillation of which, with sulphuric acid, yields a yellow acidulous liquid, possessing in an eminent degree, the characteristic odour of butyric acid. On neutralizing the solution with freshly precipitated carbonate of silver, and filtering whilst boiling, a crystalline silver salt is deposited on cooling, which is readily darkened by exposure to light, or by continued ebullition with the mother liquor. The dry salt does not detonate when heated. The potassium, barium, and lead salts, do not appear to crystallize; want of material has prevented me from determining the composition of this acid, and of its salts by analysis; considering, however, the mode of its formation, the peculiar and unmistakeable odour of butyric acid, and its yellow colour, it becomes very probable that this compound is a mixture of butyric acid, and of nitrobutyric acid.



$$HO, C_6 \left\{ \begin{matrix} H_6 \\ NO_4 \end{matrix} \right\} C_2 O_3$$

corresponding to nitro-metacetonic acid.

The following equation represents the transformation of valyl into butyric acid.

$$\underbrace{C_8\,H_9}_{\text{Valyl.}} + 5\ O = \underbrace{HO,\ (C_6\,H_7)\,C_2\,O_3}_{\text{Butyric acid.}} + HO.$$

Dry chlorine has no action on valyl in the dark, the minutest ray of light, however, suffices for the immediate production of hydrochloric acid vapours, while chlorinated substitution compounds are simultaneously formed. By an excess of chlorine the liquid gradually becomes converted into a semi-fluid almost viscid mass: direct combination of chlorine and valyl, without elimination of hydrogen does not occur under these circumstances.

The action of bromine on valyl, although less powerful, is attended with similar phenomena; iodine is dissolved in considerable quantity by it without however entering into combination; sulphur likewise has no action upon it.

The decomposition of valerianic acid into valyl and carbonic acid, with the simultaneous evolution of hydrogen is represented by the following equation:

$$\underbrace{HO,\ (C_8\,H_9)\,C_2\,O_3}_{\text{Valerianic acid.}} = \underbrace{C_8\,H_9}_{\text{Valyl.}} + 2\ CO_2 + H.$$

which is so extremely simple, that further elucidation would be superfluous were not other products formed at the same time. In order clearly to understand this peculiar reaction, we must direct our attention to the study of the two bodies occurring with it; viz.: the oxygenated constituent of the impure oil, and the odorous gas evolved with the carbonic acid. If we consider the fact of the elimination of valyl at the oxygen pole of the battery, the idea naturally suggests itself, that a partial oxidation of it into oxide of valyl may there be effected; the supposition, however, that the original oil consists of a mixture of valyl and its oxide is immediately discountenanced by its peculiar deportment with an alcoholic solution of potash, unable, as we are, to understand what kind of compound would be thus produced. The potash solution with which the oil had been boiled, when diluted with water to separate the valyl, evaporated to dryness, and distilled with sulphuric acid, was found to contain a considerable quantity of valerianic acid. The presence of this acid may be most easily explained, by assuming the existence and decomposition in the liquid, of a valerianic ether, an assumption which would lead us to consider the oxygenated constituent of the original oil as valerianate of oxide of valyl. The formation of this ether will be easily understood, if we bear in mind, that together with valyl and oxygen, valerianic acid is likewise liberated at the positive pole simultaneously with oxide of valyl in the nascent state.

It is true, that in the above decomposition by an alcoholic solution of potash, according to the analogy of the compound ethers generally, hydrated oxide of valyl should have been liberated.

If, however, and it can hardly be doubted, the hydrated oxides of amyl, valyl, and ethyl, present the same relation with reference to their miscibility with water, as do valerianic, butyric, and acetic acids, the ratios of whose solubility are inversely as their atomic weights, it is at once intelligible why, with so small a quantity of substance at my disposal, I did not succeed in separating the hydrated oxide of valyl from a liquid containing alcohol in solution.

The presence of this compound, however, was proved to a certain extent by the following observations. The alcohol containing valerianate of potash was diluted with water to separate the valyl, and distilled off from the valerianate. On introducing the first portion of the distillate into a boiling mixture of bichromate of potash and dilute sulphuric acid, a product passed over, possessing in an eminent degree the characteristic odour of both butyric and acetic acids. A further confirmation of this view of the composition of the crude oil is afforded by analysis.

The substance for investigation was repeatedly washed with water, (first with a dilute alkaline solution), dried over chloride of calcium, and distilled in vacuo at a low temperature.

0.1175 grm. of the distillate gave
0.3320 ,, ,, carbonic acid, and
0.1475 ,, ,, water.

corresponding to the following composition per cent.:

Carbon . . .	77.0
Hydrogen . .	13.8
Oxygen . . .	9.2
	100.0

If, starting with the formula $C_8\ H_9\ O, (C_8\ H_9)\ C_2\ O_3$ for the oxygenated oil, we calculate from the quantity of oxygen found, the per-centage of carbon and hydrogen belonging to this compound, we arrive at the following composition:

18 equivs.	Carbon . . .	31.0
18 ,,	Hydrogen . .	5.1
4 ,,	Oxygen . . .	9.2
		45.3

by subtracting these numbers from the above we obtain carbon and hydrogen exactly in the proportion required by the composition of valyl (C_8H_9).

	Experiment.	Theory.
Carbon . . .	46.0	46.1
Hydrogen . .	8.7	8.6

A similar mixture, prepared at a different period, when subjected to combustion gave the following numbers:

0.2647 grm. of substance gave
0.7600 ,, ,, carbonic acid, and
0.3420 ,, ,, water.

and a similar calculation leads us to the following results:

	Experimental per-centage.		Composition of valerianate of valyl.		Composition of valyl.	Theory.
Carbon	78.3	minus	25·0	=	53·3	53·4
Hydrogen	14.3		4.2		10.1	10.0
Oxygen	7·4		7·4			
	100.0		36.6		63.4	63·4

It now only remains to determine the nature of the gas evolved with carbonic acid, in the decomposition of valerianate of potash. In order to separate this gas from the vapour of valyl evaporated with it, as well as from carbonic acid, I passed it from the decomposing apparatus through a system of tubes, (*fig.* 1). *d d* is an empty tube blown out to a bulb in the lower part, and surrounded by a frigorific mixture. In this tube the larger quantity of valyl vapour is condensed, a small portion which may have escaped liquefaction being arrested in a Liebig's apparatus *g*, filled with alcohol, the vapours of which are condensed in a similar apparatus *h* containing water. The two following bulbs *k* and *l* are filled with a solution of potash, while the tube *m* contains potash in the solid form, serving, both for the separation of carbonic acid, and for the complete desiccation of the gas. . Finally, to obtain a perfect mixture, the evolved gases were collected in the gas-holder *B*, which consists of a cylinder of glass, 3 inches in diameter, and 11 inches in height, containing an inverted bell-jar, open at the lower extremity, and enclosing one vertical branch of each of the two U-shaped tubes *s* and *x*. The bell-glass is fixed by a holder in its lowest position, and the apparatus filled with mercury to such an extent, that the two tubes through which the air contained in the bell-jar is expelled, rise only a few lines above its surface. The tube *s*, moreover, at its horizontal extremity is connected by an air-tight caoutchouc joint with the tube *m*, while the branch *x* communicates in the same manner with the delivery tube *r*, which may be opened or closed at pleasure by depressing or elevating it from the mercury of the trough; both the connectors being, moreover, furnished with caoutchouc valves.

When the evolution of gases, occasioned by closing the galvanic circuit in the decomposing apparatus, had lasted nearly half an hour without interruption, and all the air contained in its different parts had evidently been expelled, the caoutchouc valve *v* was closely tied, while the holder with which the bell-jar had been depressed in the mercury, was gradually elevated as the vessel became filled with the gas generated by the decomposition. When a sufficient quantity of gas had been collected in this manner, the evolution was interrupted by breaking contact. By now tying the valve *p*, the gases contained in the gas-holder were no longer in connexion with the generating apparatus. By opening the valve *v*, and depressing the bell-jar, the quantity of gas required could easily be collected over mercury, and then transferred into the eudiometer, or into the glass balloon, for the determination of its specific gravity.

In determining the specific gravity, the following numbers were obtained:

Vol. of gas in balloon . . .	15° C.	755.9$^{\text{mm}}$	86.4 c.c.

Weight of balloon filled with gas .	15° C	771.0^{mm}	61.628 grm.
Weight of balloon filled with air .	15° ,,	771.0 ,,	61.672 ,,

From the above numbers, the specific gravity is calculated as 0.604.

In performing the eudiometrical analysis, I availed myself of the circumstance of the odorous constituent being absorbed by sulphuric acid. I therefore introduced into a measured volume of the gas a coke ball, saturated with strong fuming acid; the sulphurous acid, together with the sulphuric vapours, being subsequently removed by a moistened ball of potash.

In this manner, the following numbers were obtained:

I.

	Vol. observed.	Temp.	Bar.	Height of mercury above level in the trough.	Corrected vol. 0° C. 1^{m}. Press.
Original vol. (dry)	117.7	9.9	765.9^{mm}	65.0^{mm}	79.6
After absorption with sulphuric acid and potash (dry)	88.8	9.0	761.1 ,,	93.3 ,,	57.4

The quantity of odorous substance in the mixed gases absorbable by sulphuric acid, consequently amounts to 27.8 per cent.

The residual gas, no longer possessing any odour, and burning with a pale blue, non-luminous flame, was transferred into a eudiometer furnished with platinum wires, and exploded with oxygen, when it was found to consist of pure hydrogen.

Another portion of the above mixture, when exploded with oxygen, gave the following results:

II.

	Vol. observed.	Temp.	Bar.	Height of mercury above level in the trough.	Corrected Vol. 0° C. 1$^{\text{m}}$ Press.
Original vol. (moist).	111.8	11.0	759.4$^{\text{mm}}$	353.7$^{\text{mm}}$	42.4
After admission of oxygen (moist).	324.6	11.1	759.3 ,,	141.9 ,,	189.5
After combustion (moist).	222.7	11.1	759.0 ,,	242.3 ,,	108.4
After absorption of CO_2 (dry).	146.0	13.0	759.1 ,,	318.2 ,,	61.4

The gas remaining after the absorption of carbonic acid consisted only of pure oxygen, as had been ascertained in a previous experiment.

The above analysis leads to the following results:

	Volume of combustible gas.	Oxygen cons$^{\text{d}}$.	Carbonic acid prod$^{\text{d}}$.
	42.4 . .	85.7 . .	47.0
or			
	100.0 . .	202.1 . .	110.8

The mixture of gases under investigation containing, according to experiment II, 72.2 per cent. of hydrogen, requires 36.1 vol. of oxygen for its combustion; it is therefore evident that the remaining 27.8 vol. require 166 (=202.1—36.1) vol. of oxygen, in order to produce 110.8 vol. of carbonic acid. These numbers stand very nearly as, 1 : 6 : 4, or, in other words, 1 volume of the odorous gas requires 6 vol. of oxygen to produce 4 vol. of carbonic acid. Four vol. of carbonic acid consisting, however, of 2 vol. of carbon and 4 vol. of oxygen, and altogether 6 vol. of oxygen having disappeared, 2 vol. having evidently served for the combustion of 4 vol. of hydrogen, it is obvious that the odorous gas contains 2 vol. of carbon and 4 vol. of hydrogen condensed into one volume; hence its specific gravity is, 1.934.

2 vol. of Carbon vapour . . .	1.658
4 „ „ Hydrogen . . .	0.276
1 „ „ $C_4 H_4$	1.934

According to the above experiment, the specific gravity of a mixture of 72.2 vol. of hydrogen, and 27.8 vol. of the carbo-hydrogen, is equal to 0.604; hence it follows that the specific gravity of the latter alone is, 1.993, closely coinciding with the result of experiment.

The odorous carbo-hydrogen evolved at the positive pole in the electrolytical decomposition of valerianate of potash, according to these experiments, exhibits the composition of olefiant gas, but possesses a specific gravity double that of this compound. In this respect, it agrees with the carbo-hydrogen discovered by Faraday, and named by Berzelius *ditetryl*, with which it, in fact, appears identical by its comportment with chlorine.

If the mixed gases, washed with potash and alcohol, and collected in the gas-holder, be passed through a chloride of calcium tube into a flask (provided with three tubulures, one of which terminates in a narrow aperture), and mixed with perfectly dry chlorine, an excess being carefully excluded and light as much as possible avoided, the sides of the flask become quickly covered with oily drops, which soon collect into larger globules, and flow out from the lower aperture, while hydrochloric acid, formed by the direct combination of chlorine with the free hydrogen, is disengaged. During the whole process a slight evolution of heat is perceptible.

About half an ounce of the oily liquid, which had been collected in the vessel placed under the lower aperture of the flask, was first treated with slightly alkaline, and afterwards with pure water, in order to separate dissolved hydrochloric acid; and it was then dried over fused chloride of calcium, and subjected to a fractional distillation. The portion which boiled between 125° C. (257° F.) and 130° C. (266° F.) forming by far the larger quantity, was separately collected and purified by repeated rectifications, when a nearly constant boiling-point at 123° C. (253.4 F.) was obtained.

This compound possesses the following properties. It is a clear colourless etherial liquid, insoluble in and heavier than water. It has an agreeable sweetish odour and taste, deceptively similar to that of Dutch liquid. It dissolves with facility in alcohol and ether, and boils at the constant temperature of 123° C. (253.4 F.); mixed with alcohol it burns with a luminous smoky flame, with evolution of hydrochloric acid. Its specific gravity at 18° C. (64.4 F.) is 1.112, the density of its vapour 4.426, the latter being calculated from the following data:

Substance employed . .	0.244 grm.
Vol. of vapour observed . .	67.7 c. c.
Temperature	139.0° C.
Bar. pressure	751.0 mm.
Col. of mercury to be deducted	51.0 ,,
Pressure of oil col. at 17° C. .	366.0 ,,

By combustion with protoxide of copper the following results were obtained:

I. 0.3990 grm. of substance gave:
0.5590 ,, ,, carbonic acid, and
0.2470 ,, ,, water.
II. 0.2165 ,, ,, passed over ignited lime, dissolved in nitric acid and precipitated with nitrate of silver gave:
0.4790 ,, ,, chloride of silver.

These numbers coincide with the formula:

$$C_4\,H_4\,Cl, \text{ or } C_8\,H_8\,Cl_2.$$

	Theory.		Experiment.
8 equiv. of Carbon . .	600.0	37.8	38.2
8 ,, ,, Hydrogen .	100 0	6.3	6.8
2 ,, ,, Chlorine .	886.0	55.9	55.5
	1586.0	100.0	100.5

If we adopt, in this compound, a similar condensation of the elements, as in the oil of olefiant gas, the specific gravity of its vapour should be, 4.3837.

2 vol. of Carbon . . .	1.6584
4 ,, ,, Hydrogen . .	0.2764
1 ,, ,, Chlorine . .	2.4489
1 ,, ,, the new Chloride .	4.3837

(with this number the result of experiment 4.426 closely coincides).

It would have been extremely interesting to have studied the comportment of this compound with an alcoholic solution of potash, since its analogy to chloride of elayl justifies the expectation that, in this case, chloride of potassium, and a compound corresponding to chloride of acetyl would have been formed, the latter being represented by the formula:

$$C_8\left\{\begin{matrix}H_7\\Cl\end{matrix}\right\}$$

The small quantity of liquid at my disposal, unfortunately, did not allow me to pursue the subject any further. I must therefore confine myself to mentioning, that on heating an alcoholic solution of the compound with potash, a copious crystalline precipitate of chloride of potassium was formed, while the characteristic odour of the compound was replaced by that of a very volatile liquid, having probably the formula:

$$C_8\left\{\begin{matrix}H_7\\ Cl\end{matrix}\right\},$$

which remaining dissolved in the alcoholic solution, was precipitated, on the addition of water, in small drops, which separating at the sides of the vessel, united only with difficulty; the liquid remaining milky for a considerable period.

By the action of chlorine, on the above carbo-hydrogen, with the fluid boiling at 123° C. (253°.4 F.), higher chlorinated products are formed, even when an excess of chlorine has been carefully avoided. The slow elevation of the boiling-point from 123° C. (253°.4 F.) to 160° C. (320° F.), at once intimates that we have, in this case, other substances richer in chlorine, which possibly might have been separated by fractional distillation of a larger quantity.

The combustion of 0.3620 grm. of the product, distilling at 132° C. (269°.6 F.), gave 0.4600 grm. of carbonic acid, and 0.1800 grm. water, corresponding to the following per-centage composition:

Carbon . .	34.6
Hydrogen . .	5.5

A compound still richer in chlorine is obtained by passing the gas through pentachloride of antimony, and distilling the substance thus produced. During the process of absorption, the mixture blackened, with the evolution of hydrochloric acid. The oily product obtained was purified by repeated distillation with water, dried over chloride of calcium, and subjected to analysis, when it exhibited the following per-centage composition:

Carbon . .	28.4
Hydrogen . .	4.0
Chlorine . .	68.2

being evidently a mixture of different chlorinated compounds, whose composition may be represented by the general formula :

$$C_8\ H_{(8-x)}\ Cl_{(2+x)}$$

The opinions of chemists regarding the rational composition of the oil of olefiant gas, are, as is well known, still divided, as to whether it should be considered as the chlorine compound of a radical $C_2\ H_2$, or whether its atomic weight should be doubled, in which case it would appear as the hydrochlorate of chloride of acetyl.

$$C_4\left\{\begin{matrix} H_3 \\ Cl \end{matrix}\right\},\ H\ Cl.$$

This question must remain undecided as long as both views can still claim arguments of equal force. Now, whichever of these opinions may in future be found correct, it will evidently determine our views respecting the chemical constitution of the above chlorinated oil produced from ditetryl, or, in other words, it will decide whether we have to adopt the formula :

$$C_4\ H_4\ Cl,\ \text{or}\ C_8\left\{\begin{matrix} H_7 \\ Cl \end{matrix}\right\},\ H\ Cl,$$

as the true exponent of its rational composition. This supposition once recognised will add new force in favour of the latter mode of representation, if we bring to bear upon this case the law of Kopp respecting the regularity displayed in the boiling points of *homologous* liquids, (to employ an expression lately introduced to designate the members of such series of bodies), which, like the alcohols or the fatty acids, are represented as being derived from a starting member by the addition of *n* times $C_2\ H_2$, $C_4\ H_2$, on any other carbo-hydrogen, experiment having (within certain limits) evinced the fact that the boiling points of homologous fluids rise 19° C. (34° F.) for each additional equivalent of the carbo-hydrogen $C_2\ H_2$. The chloride of ditetryl, $C_4\ H_4\ Cl$, which boils at 85° C. (185° F.), differing from chloride of elayl by one equivalent of the carbo-hydrogen $C_2\ H_2$, should boil at 104° C. (219°.2 F.); on doubling, however, the atomic weight of the two bodies, (chloride of elayl $C_4\ H_4\ Cl_2$, and chloride of ditetryl $C_8\ H_8\ Cl_2$), their elementary difference becoming equal to 2 $(C_2\ H_2)$, the boiling point of the latter should be 123° C. (253°.4 F.), which is the temperature actually observed by experiment. Although this observation cannot be considered as a direct argument for the assumed molecular arrangement, I consider it nevertheless of sufficient weight to assist in the ultimate decision of the question regarding the atomic constitution of the two compounds.

We find no difficulty in explaining the formation of the carbo-hydrogen $C_4\ H_4$, or $C_8\ H_8$, from valerianic acid; like the valerianate of the oxide of valyl, it is evidently a secondary product of the decomposition of valyl, and most probably formed by the action of the oxygen separating along with valyl, at the positive pole. We may assume that, under the influence of this oxygen, valyl is deprived of one equivalent of hydrogen, yielding one equivalent of ditetryl and one equivalent of water.

The action of electrolized oxygen, on a solution of valerianate of potash, therefore gives rise to three distinct phenomena:

1st. A decomposition of the acid into valyl and carbonic acid:

$$\underbrace{HO, (C_8\ H_9)\ C_2\ O_3}_{\text{Valerianic acid.}} + O = \underbrace{C_8\ H_9}_{\text{Valyl.}} + 2\ CO_2 + HO.$$

2ndly. The decomposition of valyl into ditetryl and water:

$$\underbrace{C_8\ H_9}_{\text{Valyl.}} + O = 2\ \underbrace{(C_4\ H_4)}_{\text{Ditetryl.}} + HO.$$

3rdly. A direct oxidation of valyl into oxide of valyl, which combines in the nascent state with free valerianic acid.

$$\underbrace{C_8\,H_9}_{\text{Valyl.}} + O + \underbrace{(C_8\,H_9)\,C_2\,O_3}_{\text{Valerianic acid.}} = \underbrace{C_8\,H_9\,O,\,(C_8\,H_9)\,C_2\,O_3}_{\text{Valerianate of oxide of valyl.}}.$$

The two latter processes appear to take place simultaneously, though perfectly independent of each other. I have not, however, succeeded in exactly ascertaining the circumstances which favour the formation of the one or the other.

ELECTROLYSIS OF ACETIC ACID.

The remarkable analogy of the series of acids $(C_2\,H_2)_n + O_4$, induced me to believe that acetic acid would undergo a similar decomposition to valerianic acid, yielding, by absorption of one equivalent of oxygen, methyl and carbonic acid:

$$\underbrace{HO\,(C_2\,H_3)\,C_2\,O_3}_{\text{Acetic acid.}} + O = \underbrace{C_2\,H_3}_{\text{Methyl.}} + 2\,CO_2 + HO.$$

In a preliminary experiment, it was found that on decomposing a concentrated solution of acetate of potash, gaseous products only were evolved, consisting of carbonic acid, hydrogen, a combustible inodorous gas, and a compound possessing a peculiar etherial odour, and absorbable by sulphuric acid. In the investigation of these gaseous products, I availed myself of the same decomposing apparatus as was employed in the decomposition of valerianic acid; the evolved gases were first passed through a series of bulb tubes containing potash, afterwards through a tube filled with sulphuric acid (for the absorption of the odorous gas), and finally made to pass through a tube containing pieces of fused hydrate of potash, previous to collection in a gas-holder. In this operation it is necessary to employ a very concentrated solution of the potash salt perfectly free from chloride of potassium, the smallest trace of the latter giving rise to the formation of chloride of methyl, which is easily recognisable by the green-bordered flame with which it burns when inflamed in contact with the air.*

When the evolution of gas had continued for about an hour, and had entirely displaced all traces of atmospheric air contained in the system of tubes and the gasometer, I filled the latter by gradually raising the bell, the delivery tube dipping under the mercury. The apparatus being too small to allow a sufficient quantity of gas being collected for taking its specific gravity, for eudiometrical analysis, and for combustion with protoxide of copper, the bell-jar was again fixed before being completely filled, and the gas issuing from the tube *r* was collected in a flask, for the determination of the specific gravity.

The contents of the gasometer were now easily confined by tying the caoutchouc valves *p* and *v* over the inserted glass rods, after the collection of gas had ceased from the interruption of the galvanic current.

In determining the relative proportion of carbon and hydrogen, an ordinary combustion-tube, open at both ends, was employed; when filled with freshly ignited protoxide of copper, the anterior extremity was connected with the usual potash bulbs and chloride of calcium tube, the posterior end being attached by a caoutchouc tube to the gasometer. After opening the caoutchouc valve *v*, the silken cord was untied, and by gently depressing the bell-jar, a continuous stream of gas passed over the ignited protoxide of copper, until a sufficiency of carbonic acid and water had been collected, when the caoutchouc valve was again closed. The posterior tube connected with the gas-holder was now cut, in order to allow of the removal of the carbonic acid remaining in the apparatus.

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* In a similar manner various other secondary products are formed, a mixture of valerianate of potash and chloride of potassium, for example, produces in the place of valyl, a chlorinated, etherial compound; a disagreeably smelling compound is obtained by exposing a mixture of acetate of potash and sulphide of potassium to the action of a galvanic current, the anode being formed of a platinum plate.

The following are the numbers obtained:

Carbonic acid . .	0.2470
Water	0.2635

corresponding to a ratio of 1 equivalent of carbon to 2.06 equivs. of hydrogen, or of 1 volume of carbon vapour to 5.2 vols. of hydrogen.

The specific gravity of the gas collected in a small flask over mercury was found to be 0.403.

	Temp.	Pressure.	
Volume of gases in flask	19.3°C.	749.2^{mm}	211.3 cc.
Mercury column to be deducted . . .	...	15.0 „	...
Weight of flask filled with gas	22.0°C.	749.0 „	46.669 grm.
Weight of flask filled with air	—	—	46.819 „

The further data for the composition of the gas were obtained by eudiometrical analysis, which exhibited the presence of a minute quantity of oxygen.

	Observed.	Temp. C°.	Bar.	Height of mercury column.	Corrected vol. 0° C. and 1^{m} pressure.
Volume of gas employed (moist).	137.3	19.3	747.2^{mm}	31.5^{mm}	89.6
After absorption of oxygen (moist).	132.0	19.0	740.0 „	35.9 „	86.9

The quantity of oxygen, therefore, amounts to 3 per cent. The residuary gas was transferred into a larger eudiometer, and detonated with oxygen in experiments II *a* and II *b*, the following numbers were obtained :

II *a*.

	Observed vol.	Temp. C°.	Barom.	Height of mercury column.	Corrected vol. 0° C. and 1^{m} pressure.
Volume of gas employed (moist).	200.0	18.0	749.0^{mm}	373.4^{mm}	67.6
After admission of oxygen (moist).	475.9	17.4	751.2 ,,	92.3 ,,	287.6
After combustion (moist).	345.6	18.0	751.1 ,,	225.6 ,,	165.4
After absorption of carbonic acid (dry).	283.2	17.7	748.8 ,,	288.6 ,,	122.3
After admission of hydrogen (dry).	574.5	17.8	747.5 ,,	6.0 ,,	399.0
After combustion (moist).	114.2	17.4	748.9 ,,	460.2 ,,	29.4

II *b*.

	Observed vol.	Temp. C°.	Barom.	Height of mercury column.	Corrected vol. 0° C. and 1^{m} pressure.
Volume of gas employed (moist).	91.8	18.9	740.2 ,,	476.3 ,,	21.26
After admission of oxygen (moist).	410.2	19.0	740.3 ,,	153.7 ,,	218.7
After combustion (moist).	366.2	19.0	740.4 ,,	197.1 ,,	180.43
After absorption of carbonic acid (dry).	341.4	18.0	744.0 ,,	222.1 ,,	167.15

		Vol. of gases used.	Oxygen consumed.	Carbonic acid generated.
Experiment II *a*	.	67.6	97.7	43.1
Experiment II *b*	.	21.26	30.3	13.3

In calculating these numbers for a mixture of hydrogen and methyl, we find that in both experiments a smaller quantity of oxygen has disappeared than is required for the perfect combustion of such a mixture.

This circumstance appears to point out the presence of oxide of methyl, which accompanies methyl itself in pretty constant proportion. In designating the quantity of combustible gas employed by *A*, the oxygen which has disappeared by *B*, the carbonic acid produced in combustion by *C*; and further, the quantity of oxygen, methyl, and of oxide of methyl, respectively by x, y, and z, we arrive at the following equation,

$$\begin{aligned} x + \quad y + .\ z &= \mathrm{A} \\ \tfrac{1}{2}x + 3\tfrac{1}{2}\,y + 3\,z &= \mathrm{B} \\ 2\,y + 2\,z &= \mathrm{C} \end{aligned}$$

by which we obtain for x, y, and z, the following values:

$$x = \frac{2\,\mathrm{A} - \mathrm{C}}{2}$$

$$y = \frac{4\,\mathrm{B} - 2\,\mathrm{A} - 5\,\mathrm{C}}{2}$$

$$z = \mathrm{A} + 3\,\mathrm{C} - 2\,\mathrm{B}.$$

If we now substitute for A, B, and C, the numerical values found, we arrive at the following composition for the two consumed volumes of gas (Exp. II *a* and II *b*):

		Experiment II *a*.	Experiment II *b*.
Hydrogen	. . .	46.1	14.60
Methyl	. . .	20.0	6.10
Oxide of methyl	. .	1.5	0.56
Total volume	.	67.6	21.26

Hence, from experiments I. and II., results the following per-centage composition of the mixed gases :

	I.	II.
Oxygen . . .	3.0	3.0
Hydrogen . .	66.0	66.6
Methyl . . .	28.8	27.8
Oxide of methyl .	2.2	2.6
	100.0	100.0

The specific gravity of a gaseous mixture of this composition would be 0.4123 which closely coincides with the numbers found by experiment, 0.403. This composition receives further confirmation from the relative proportions of carbon and hydrogen, obtained by combustion with protoxide of copper.

		Carbon vapour.	Hydrogen.
28.8 vol. Methyl	contain	28.8 vol.	86.4 vol.
2.2 ,, Oxide methyl	,,	2.2 ,,	6.6 ,,
66.0 ,, Hydrogen	,,	— ,,	66.0 ,,
The gaseous mixture		31.0	159.0 ,,

Being the ratio of 31.0 vol. of carbon vapour to 159.0 vol. of hydrogen, or of 1 vol. of carbon vapour to 5.13 vol. of hydrogen, very closely coinciding with the above experimental ratio of 1 : 5.21.

I have before mentioned, that the gases evolved in the electrolysis of acetic acid, contain a gas which is absorbable by sulphuric acid. Independently of the remarkable odour of acetate of methyl which this gas possesses, the supposition that acetate of methyl is actually obtained among the products of the decomposition of acetic acid, receives some support from the analogous decomposition of valerianic acid. With the view of ascertaining the per-centage of this body in the mixture of gases, and to study its nature, I repeated the above experiments with a portion of gas which had not previously been passed through sulphuric acid, and which consequently still contained the odorous principle; it burned like the other, with a feebly luminous, bluish flame.

An indefinite volume being passed from the gas-holder over ignited protoxide of copper, gave:

0.249 grm. of carbonic acid, and
0.247 ,, ,, water.

Corresponding to the ratio of:

1 vol. of carbon vapour, and
4.851 vols. of hydrogen.

The specific gravity of the mixture was found to be 0.4373, as is seen by the following experiment:

	Temp. C.	Pressure.	
Volume of gas in flask .	18.0°	741.0^{mm}	211.7 cc.
Weight of flask filled with gas	19.0°	749.0 ,,	42.4065 grm.
Weight of flask filled with air	—	—	42.5500 ,,

To ascertain the per-centage of free oxygen and of the odorous constituent, I first determined, in a measured volume, (experiment III), the quantity of the latter by absorption with a coke ball saturated with sulphuric acid, and subsequently the amount of oxygen, by introducing a ball of phosphorus. The remaining portion of combustible gas was then detonated with oxygen in a large eudiometer, (experiment IV).

III.

	Observed vol.	Temp. C.	Bar.	Height of mercury column.	Corrected vol. 0° C. and 1^{m} pressure.
Volume of gas used (moist).	116.4	17.8	747.2^{mm}	21.2^{mm}	77.67
After absorption with sulphuric acid (dry).	113.8	17.9	746.0 ,,	24.8 ,,	77.03
After absorption of oxygen (dry).	113.0	17.6	746.0 ,,	25.1 ,,	76 5

IV.

Volume of gas free from oxygen and odorous constituent (moist).	190.6	17.8	746.0 ,,	378.2 ,,	63.1
After admission of oxygen (moist).	373.9	17.9	744.7 ,,	192.4 ,,	188.4
After combustion (moist).	208.6	18.0	743.8 ,,	339.6 ,,	72.17
After absorption of carbonic acid (dry).	105.3	18.2	745.9 ,,	465.7 ,,	27.66
After admission of hydrogen (dry).	311.5	18.0	750.6 ,,	255.7 ,,	144.63
After combustion (dry).	182.6	18.1	750.6 ,,	386.5 ,,	62.35

According to the latter experiment, it follows that 63.1 vols. of gas previously treated with sulphuric acid and phosphorus, require for combustion 97.4 volumes of oxygen, giving rise to the formation of 44.51 vols. of carbonic acid. If we now calculate these numbers according to the above equation for hydrogen, methyl, and oxide of methyl, we find that the original 63.1 vols. contained 40.85 vols. of hydrogen, 20.9 vols. of methyl, and 1.35 vol. of oxide of methyl. From these data, and likewise from the results of experiment III, we obtain the following per-centage composition of the mixture, in which the gas absorbable by sulphuric acid is enumerated as acetate of methyl.

Oxygen	0.7
Hydrogen . . .	63.8
Methyl	32.6
Oxide of methyl . .	2.1
Acetate of methyl . .	0.8
	100.0

The specific gravity of such a mixture should be 0.4430, which does not far differ from experimental results, the number obtained being 0.4370.

	Volume per-cent.		Specific gravity.		Weight.
Oxygen . .	0.7	×	1.1092	=	0.7647
Hydrogen . .	63.8	×	0.0691	=	4.4086
Methyl . .	32.6	×	1.0365	=	33.7899
Oxide of methyl .	2.1	×	1.5893	=	3.3375
Acetate of methyl	0.8	×	2.5567	=	2.0454

$$\frac{44.3461}{100} = 0.443$$

If we calculate the relative volumes of carbon and hydrogen contained in this mixture of gases, we obtain the following numbers:

		Carbon vapour.	Hydrogen.
63.8 vol. H	containing	—	63.8 vol.
32.6 ,, C_2H_3	,,	32.6 vol.	97.8 ,,
2.1 ,, C_2H_3O	,,	2.1 ,,	6.3 ,,
0.8 ,, $C_2H_3O, \overline{A}$	,,	1.2 ,,	2.4 ,,
Being a proportion of		35.9 to	170.3 ,,

or of one volume of carbon vapour to 4.74 vols. of hydrogen, which coincides with the results obtained by combustion with protoxide of copper, viz.: 1 vol. of carbon vapour to 4.85 vol. of hydrogen. The per-centage composition gains additional support by the eudiometrical analysis of the same gas, which still contained the odorous principle, but which was previously freed from oxygen.

The following numbers were obtained:

	Observed vol.	Temp. C.	Barom.	Height of mercury column.	Corrected vol. 0° C. and 1^m pressure.
Volume of gas used (moist).	138.0	18.2	750.5^{mm}	432.6^{mm}	39.11
After admission of oxygen (moist).	360.6	18.3	750.2 ,,	206.4 ,,	178.5
After combustion (moist).	263.9	18.2	750.1 ,,	303.9 ,,	106.8
After absorption of carbonic acid (dry).	213.9	18.2	748.4 ,,	354.0 ,,	78.9

In the combustion of 39.1 vols. of this gas 60.5 vols. of oxygen are consumed, giving rise to the formation of

27.9 vols. of carbonic acid. By now calculating the quantity of oxygen necessary for the combustion of 63.8 vols. of hydrogen, 32.6 vols. of methyl, 2.1 vols. of oxide of methyl, and 0.8 vol. of acetate of methyl, and likewise taking into consideration the amount of carbonic acid produced, we arrive at results but slightly differing from the numbers obtained by experiment:

Vols.			Oxygen vols.		Carbonic acid vols.
63.8 H	requiring for	combustion	31.9	and producing	—
32.6 $C_2 H_3$	,,	,,	114.1	,,	65.2
2.1 $C_2 H_3 O$	,,	,,	6.3	,,	4.2
0.8 $C_2 H_3 O, \bar{A}$	,,	,,	2.8	,,	2.4
99.3 mixed gases	=		155.1		71.8

or that 39.1 vols. require for combustion 61.0 vols. of oxygen (experimental result, 60.5 vols.), producing 28.2 vols. of carbonic acid (experimental result, 27.9).

These facts sufficiently prove that the quantity of the compound imparting the peculiar etherial odour to the gases, which are evolved in the electrolytical decomposition of acetate of potash, is so small, that if, as experiment seems to point out, it actually consists of acetate of methyl, it becomes almost impossible to condense it by a low temperature. An experiment made with this view was, indeed, perfectly unsuccessful. The ready absorption of this body, by sulphuric acid, agrees with the comportment of acetate of methyl; the acid employed in the experiment assumed a yellowish tint, and darkened on the application of heat, with the evolution of acetic and sulphurous acid vapours.

The above experiments had been completed, when I became aware that a gaseous mixture, consisting of one-third methyl and two-thirds of hydrogen, possesses the same specific gravity as is exhibited by a mixture of two-thirds of marsh-gas, and one-third of hydrogen, and moreover, both mixtures contain the same relative amounts of carbon and hydrogen, and consequently consume, not only an equal volume of oxygen in their combustion, but produce the same quantity of carbonic acid; and hence the facts observed in the electrolysis of acetic acid might lead to the assumption, that the gases evolved in its electrolytical decomposition consist of hydrogen and marsh-gas. With the view of removing all doubt on this point, I have endeavoured to prepare methyl in a state of purity: I availed myself for this purpose, of the decomposing apparatus already described, which allows us to collect with facility the products liberated at either pole.

The interior cell containing the platinum plate was closed for this purpose with the cork, which besides the platinum wire for producing contact, contained, moreover, the delivery tube through which the generated gases were evolved, in order to be conducted through two bulb-tubes filled with concentrated solution of potash, and afterwards through a similar vessel containing sulphuric acid (for the absorption of water and acetate of oxide of methyl) and subsequently collected in the gas-holder. After every trace of atmospheric air had been expelled, the collected gas contained, nevertheless, a small quantity of carbonic acid, the two potash bulbs not having been sufficient to absorb the carbonic acid, which had been evolved from the separated cell in much larger proportion than in the former arrangement, because, in the former experiment, the simultaneous liberation of acetic acid at the positive pole effectually prevented the formation of a carbonate.

The eudiometrical analysis of the mixture which, as special experiment had proved, did not contain free oxygen, gave the following results:

VI.

	Observed vol.	Temp. C.	Barom.	Height of mercury column.	Corrected vol. 0° C. and 1^{m} pressure.
Volume of gas used (moist).	121.9	17.3	738.6^{mm}	18.2^{mm}	80.9
After absorption of carbonic acid (dry).	90.9	17.2	744.8 ,,	44.9 ,,	59.86

VII.

Gas used (moist).	114.1	17.5	744.9^{mm}	457.4^{mm}	29.23
After admission of oxygen (moist).	452.0	17.5	745.2 ,,	115.7 ,,	261.1
After combustion (moist).	374.0	17.6	745.2 ,,	192.5 ,,	188.9
After absorption of carbonic acid (dry).	293.5	17.5	746.0 ,,	273.6 ,,	130.5

According to these observations the gaseous mixture contains 26.0 of carbonic acid, and 74.0 of combustible gas, of which (experiment VII) 29.23 vols. require 101.37 vols. of oxygen for complete combustion, producing 58.4 vols. of carbonic acid, which closely corresponds with the ratio, 1 : 3½ : 2 ; hence it appears that the gas evolved with carbonic acid, at the positive pole, is actually methyl, containing not even a trace of marsh-gas, which requires the double volume of oxygen for its complete combustion, and produces only an equal volume of carbonic acid.

The experimental numbers correspond with the following per-centage:

Carbonic acid . .	26.0
Methyl . . .	69.3
Oxide of methyl . .	4.7
	100.0

The specific gravity of such a mixture is 1.188, a number closely coinciding with the result of experiment, which gave 1.172, as the following data will shew:

	Temp.	Barometer.	
Volume of gas in flask	17.3°	717.6	212 c. c.
Weight of flask filled with gas	17.2°	738.6	53.826 grm.
,, ,, air	—	—	53.796 ,,

The gas remaining after the absorption of carbonic acid (experiment VI), which is methyl mixed with traces of oxide of methyl, possesses the following properties: it is inodorous * and tasteless, insoluble in water, and burns with a bluish non-luminous flame; alcohol dissolves an equal volume, absorbing it without residue; neither sulphuric acid nor pentachloride of antimony dissolve it, and hence it corresponds, in all its properties, to the gas obtained from cyanide of ethyl.†

Methyl may be distinguished from marsh-gas, to which it is in some respects very similar, both by its solubility in alcohol, and its comportment with an excess of chlorine gas, by which methyl is converted into sesquichloride of carbon, while marsh-gas is transformed into the bichloride.

In conclusion, I may observe, that on employing two

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* The feebly etherial odour of the gas prepared from cyanide of ethyl evidently arises from traces of cyanide of ethyl.

† Ann. der Chem. und Pharm. Bd. LXV. S. 269.

decomposing cells, the gas evolved at the positive pole does not contain carbonic acid, but consists of pure hydrogen.

According to the observations I have communicated, acetic acid, when decomposed in the circuit of the voltaic current, is decomposed into methyl and carbonic acid, both being liberated at the positive pole, whilst at the negative pole, pure hydrogen only is evolved. It further appears, that a small quantity of methyl is converted into the oxide. On leaving out of consideration the small quantity of the latter, one equivalent of acetic acid should accordingly yield 2 vols. of hydrogen, 2 vols. of methyl, and 4 vols. of carbonic acid, as is shown in the following equation :

$$\mathrm{HO,\ (C_2\,H_3)\ C_2\,O_3} = \left\{ \begin{array}{ll} \mathrm{H} & \text{2 vols.} \\ \mathrm{C_2\,H_3} & \text{2 vols.} \\ \mathrm{2\ C\,O_2} & \text{4 vols.} \end{array} \right.$$

The gases evolved from the decomposing cell, in the decomposition of acetate of potash, should therefore consist of equal volumes of methyl and hydrogen ; as, however, experiments II, IV, and V, show that nearly double the amount of hydrogen is evolved, without an equivalent proportion of oxygen being liberated, we are led to the conclusion, that together with the above-mentioned transformations a simultaneous decomposition of water takes place, whose oxygen (considerably surpassing the amount contained in the oxide of methyl) evidently oxidizes a portion of the liberated methyl completely into carbonic acid and water ; from this fact, however, it would follow, that carbonic acid would be produced in much larger proportion compared with methyl, than is indicated by the foregoing formula. With the view of deciding this question, I have investigated the mixture of carbonic acid and methyl, evolved at the positive pole, which had been previously freed from acetic vapours which might have been carried over, by passing the gas through a bulb-tube containing water.

VIII.

	Observed vol.	Temp. C.	Barom.	Mercury column.	Corrected vol. 0° C. and 1^{m} pressure.
Volume of gas (moist).	110.2	17.0	764.0^{mm}	25.3^{mm}	73·27
After absorption of carbonic acid (dry).	35·3	15·8	753·3 "	99·0 "	21.96

The gaseous mixture under investigation was found to contain 21.96 vols. of methyl and 51.31 vols. of carbonic acid; or, in other words, for every volume of the former, there are 2½ volumes of the latter, instead of 2 volumes, as indicated by the above equation.

These observations appear sufficient to prove, that in the electrolysis of acetic acid, even when employed in the form of a concentrated solution of its potash salt, a simultaneous decomposition of water takes place, which may perhaps be partially or entirely avoided by modifying the electrical current.

ON THE ELECTROLYSIS OF ACETIC ACID.*

HAVING twenty years ago resolved acetic acid into carbonic acid and methyl, by the electrolysis of the aqueous solution of its potassium salt, I further examined the behaviour of free acetic acid towards oxygen evolved by electrolysis, in the hope of thereby oxidising it to glycollic or dioxyacetic acid.

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* [From The Journal of the Chemical Society of London, Vol. 21 (1868), pp. 195-196.]

I have lately resumed these experiments, using as the electrolyte, glacial acetic acid, mixed with just enough water and sulphuric acid to render it capable of conducting the galvanic current. For electrodes, I used two platinum plates, which were immersed in the liquid without any separating diaphragm, and the liquid was kept cool during the electrolysis.

If, after the action of the current has been continued for twelve hours, the liquid be freed from sulphuric acid by baryta-water, and then evaporated, there remains a small quantity of a viscid non-volatile substance, which exhibits strong acid properties, and crystallises slowly over oil of vitriol.

My expectation that this acid might be glycollic acid has not been realised. Its behaviour, and more especially the properties of its salts, are quite distinct from those of glycollic acid, and yet its calcium salt has exactly the composition of glycollate of calcium.

The quantity of this acid obtained being always very small, I have not hitherto been able to analyse any of its other salts.

If the further investigation of this interesting acid should establish its isomerism with glycollic acid, the result might, perhaps, tend to support the assumption that the four hydrogen atoms of marsh gas, or the three hydrogen atoms of methyl, are not of equal value.

Alembic Club Reprints—No. 16

PAPERS ON
ETHERIFICATION
AND ON
THE CONSTITUTION OF SALTS

BY

ALEXANDER W. WILLIAMSON, LL.D., F.R.S.

(1850-1856)

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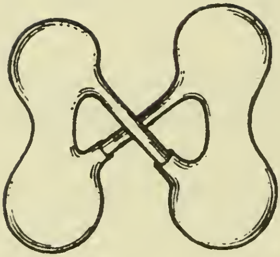

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PREFACE.

THE papers reprinted here form a group of great interest to the student of the historical progress of chemistry. They date from a period at which the development of synthetic organic chemistry was only beginning to occupy the attention of chemists to any considerable extent, and they deal with a number of questions which were matters of controversy at that period. The most important of these questions were undoubtedly those concerning the theory of etherification, and the true relationships of alcohol and ether to each other, and of both to water. It is in regard to his elucidation of these questions in particular that the name of their distinguished author, as that of one of the pioneers in the foundation of modern organic chemistry, will always be intimately connected with the history of chemistry.

In the cases of two papers which were communicated to meetings of The British Association, it has been considered advisable to reprint the short abstracts which appeared in the Reports of these meetings as well as the full papers, which were published elsewhere.

It is a matter of much gratification to the Club that the reproduction of these papers is made during the life-time and with the consent of their author. For the kindly-expressed permission to reprint them, the Club returns grateful thanks to Dr Williamson.

L. D.

RESULTS OF A RESEARCH ON ÆTHERIFICATION.*

THE process by which this remarkable transformation of the elements of alcohol is effected has been the subject of much discussion among chemists ; of the two theories which have been devised to explain it, each counts among its supporters many first-rate chemists.

The facts upon which the contact theory lays peculiar stress are more physical than those to which the appropriately-designated chemical theory refers for its evidence. But there is one point upon which the two differ essentially, and that is the composition of alcohol ; the one maintaining that the two products, æther and water, are made from 2 atoms of alcohol ; the other, that they are both produced from 1 atom of double size. This is a difference of fact, and is therefore susceptible of being decided by experiment, as it requires nothing more than a direct evidence of the relative atomic weights of alcohol and æther.

An experiment was accordingly devised, of such a nature as to give a result according to the simple, differing from that according to the double atomic weight of alcohol. It consisted in making æther from alcohol by a new process, in which the various steps of which it consists were performed separately. One-sixth of the hydrogen of alcohol was first expelled by the action of potassium ; this compound differs from æther by having half as much carburetted hydrogen as that body to an equivalent weight of potassium to the other half, or by doubling its atomic weight, may be supposed to contain æther and potash. By double decomposition with iodide of æthyle, this substance was converted into æther, and not into a body of double the atomic weight of æther, which would have been the case according to the chemical theory of ætherification. By acting upon the same potassium compound with other iodides, new æthers were obtained, which to 1 atom of oxygen contained two different carburetted hydrogen atoms, one of which was contained in the alcohol, the other occupied the place of the hydrogen of that body.

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* [From *Report of the Twentieth Meeting of the British Association for the Advancement of Science*, 1850, part 2, p. 65.]

In the common process of ætherification, sulphovinic acid is known to be the immediate product of the action of the sulphuric acid upon the alcohol. Now this sulphovinic acid is strictly analogous to iodide of æthyle and iodide of hydrogen. To convert alcohol into æther, it has merely to exchange its æthyle for the hydrogen, which in the preceding experiment was expelled by potassium. It is thus reconverted into sulphuric acid, to recommence a similar circle.

The continuous action of the reagent sulphuric acid, of which a given quantity is known to be capable of converting an unlimited amount of alcohol into æther and water, is thus owing to an exchange of analogous molecules in alternately opposite directions, and is distinctly different from any effect of chemical affinity.

THEORY OF ÆTHERIFICATION.* †

WHEN sulphuric acid is brought in contact with alcohol under certain circumstances, a new arrangement is effected in the elements of the alcohol, which divide into two groups, forming æther and water. Now it is well known that the process by which this change is effected may be represented in two ways, the difference of which consists in their respectively selecting for starting-point a different view of the constitution of alcohol. According to the one view, an atom of alcohol weighs 23, and is made up of $C^2 H^6 O$; so that to form æther, two atoms of it are needed, one of which takes $C^2 H^4$ from the other, setting free the water with which these elements were combined ; whereas, according to the other view, alcohol weighs 46, and *contains* æther and water. These are not the only points of difference which are urged ; but they are the most real and tangible, and their consideration is sufficient for our present purpose. If by any direct fact we could decide which of these two expressions is the correct one, the ground would be clear for an examination of the process of ætherification itself. In order to show more clearly the true meaning of the facts I have to adduce on this point, I will bring them before you in the order in which they arose.

My object in commencing the experiments was to obtain new alcohols by substituting carburetted hydrogen for hydrogen in a known alcohol. With this view I had recourse to an expedient, which may render valuable services on similar occasions. It consisted in replacing the hydrogen first by potassium, and acting upon the compound thus formed by the chloride or iodide of the carburetted hydrogen which was to be introduced in the place of that hydrogen. I commenced with common alcohol, which, after careful purification, was saturated with potassium, and as soon as the action had ceased, mixed with a portion of iodide of æthyle equivalent to the potassium used. Iodide of potassium was readily formed on the application of a gentle heat, and the desired substitution was effected ; but, to my astonishment, the compound thus formed had none of the properties of an alcohol —it was nothing else than common æther, $C^4H^{10}O$.

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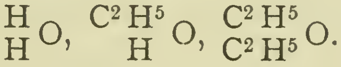
* [From *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, [3] vol. xxxvii., (1850), pp. 350-356.]

† Communicated by the Author ; having been read before the British Association at Edinburgh August 3, 1850.

Now this result at once struck me as being inconsistent with the higher formula of alcohol ; for if that body contained twice as many atoms of oxygen as are in æther, I ought clearly to have obtained a product containing twice as much oxygen as æther does. The alternative was evident ; for having obtained æther by substituting C^2H^5 for H in alcohol, the relative composition of the two bodies is represented *by expressing that fact in our formula.* Thus alcohol is $\begin{matrix}C^2H^5\\H\end{matrix}O$, and the potassium compound is $\begin{matrix}C^2H^5\\K\end{matrix}O$; and by acting upon this by iodide of æthyle, we have

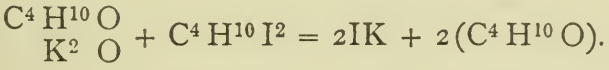
$$\begin{matrix}C^2H^5\\K\end{matrix}O + C^2H^5I = IK + \begin{matrix}C^2H^5\\C^2H^5\end{matrix}O.$$

Of course the proportion between the two bodies is the only point upon which I here enter, and the same reasoning would be applicable to any multiple of the formulæ assumed. Some chemists may perhaps prefer doubling them in order to avoid the use of atoms of hydrogen, potassium, &c.; but I have not felt myself justified in doing so, because that would involve doubling the usual formula for water; for, as I will presently show, water is formed in ætherification by replacing the carburetted hydrogen of alcohol by hydrogen, which, of course, obliges us to assume the same unity of oxygen in both. Alcohol is therefore water in which half the hydrogen is replaced by carburetted hydrogen, and æther is water in which both atoms of hydrogen are replaced by carburetted hydrogen: thus,



$$\begin{matrix}H\\H\end{matrix}O,\quad \begin{matrix}C^2H^5\\H\end{matrix}O,\quad \begin{matrix}C^2H^5\\C^2H^5\end{matrix}O.$$

This formation of æther might however be explained after a fashion by the other theory — by supposing the potassium compound to contain æther and potash, which separate during the action of the iodide of æthyle; so that half the æther obtained would have been contained in that compound, and the other half formed by double decomposition between potash and iodide of æthyle: thus—



$$\begin{matrix}C^4H^{10}O\\K^2\ O\end{matrix} + C^4H^{10}I^2 = 2IK + 2(C^4H^{10}O).$$

But although the insufficiency of this explanation becomes evident on a little reflection, I devised a further and more tangible method of arriving at a conclusion. It consisted in acting upon the potassium compound by iodide of methyle, in which case I should, if that compound were æther and potash, obtain a mixture of æther and oxide of methyle; whereas in the contrary case I should obtain a body of the composition C^3H^8O. Now this substance I obtained, and neither æther nor oxide of methyle.

In this experiment the two theories cross one another, and must lead to different results; for it is evident that, in the first-mentioned decomposition by which æther was formed, the only difficulty in explaining the process decisively consisted in our inability to prove that the carburetted hydrogen introduced instead of the hydrogen did not have in the product an atom of oxygen to itself, but that, on the contrary, it was coupled with the carburetted hydrogen already contained in the alcohol—the two in combination with one atom of oxygen. It is clear that if alcohol *contain* æther and water, and the carburetted hydrogen in my first experiment formed a second atom of æther by taking the place of the hydrogen of this water, that the process being the same in the second experiment, we should then have obtained two æthers. Whereas if the formation of æther from alcohol be effected by synthesis, a new carburetted hydrogen being added to the one already contained in the alcohol, we ought to obtain the new intermediate æther which I obtained.

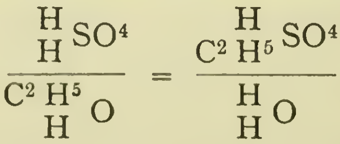
The complete description of this remarkable body and of its decompositions, will form the subject of a future paper. I will now merely state that its boiling-point is a little above 10° Cent.; it is possessed of a very peculiar smell, distinctly different from that of common æther; and, like that body, it is only slightly soluble in water. It is not acted upon by the alkali-metals at the common atmospheric temperature.

By acting upon the potassium-alcohol in like manner by iodide of amyle, I effected a similar substitution of the elements of that carburetted hydrogen in the place of the hydrogen of alcohol, and obtained an æther boiling at 111° C., having the composition $C^7 H^{16} O$. There is some reason to believe that this body is the same which Balard obtained by decomposition of chloride of amyle by an alcoholic solution of hydrated potash, and which that distinguished chemist took for oxide of amyle.

From the perfect analogy of properties between the known terms of the alcoholic series, it was to be expected that similar substitutions might be effected in the others ; and I have verified this by experiment. Of course the formulæ of the other alcohols must be reduced to half, for the same reasons as that of common alcohol. Methylic alcohol is therefore expressed by the formula $\begin{matrix}CH^3\\H\end{matrix}O$, as common alcohol is $\begin{matrix}C^2H^5\\H\end{matrix}O$; and in the same manner amylic alcohol is $\begin{matrix}C^5H^{11}\\H\end{matrix}O$, and the same of the higher ones. In conformity to this fact, we must be able to obtain the same intermediate æthers by replacing hydrogen in these alcohols (methylic and amylic) by the carburetted hydrogen of iodide of æthyle, as by the inverse process described above. This I have verified in the case of the three-carbon æther, which may be obtained indifferently by replacing one-fourth of the hydrogen of methylic alcohol by C^2H^5, or by replacing one-sixth of the hydrogen of common alcohol by CH^3. Its rational formula is therefore $\begin{matrix}C^2H^5\\C\ H^3\end{matrix}O$.

By acting upon the compound $\begin{matrix}CH^3\\K\end{matrix}O$ by iodide of amyle, I obtained a third æthereal compound, of which the formula is $\begin{matrix}C\ H^3\\C^5H^{11}\end{matrix}O$. This is evidently the only one of the three new æthers, which, containing an even number of carbon atoms, might be conceived to have been formed from one alcohol ; but when treated with monobasic acids, as hydrochloric, it cannot be expected to act in the same manner as its homogeneous isomeric, the æther $\begin{matrix}C^3\,H^7\\C^3\,H^7\end{matrix}O$ of the three-carbon alcohol $\begin{matrix}C^3\,H^7\\H.\end{matrix}O$; but of this I will give an exact account in the paper above alluded to.

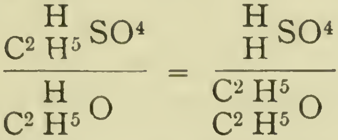
My task is now to explain the process of ætherification by the action of sulphuric acid ($SO^4\,H^2$) upon alcohol; and in order to accomplish that, I must show the connexion between those substances and the reagents used in the above-described experiments. With this view, I have merely to add to the above facts the acknowledged analogy of the simple and compound radicals in their compounds. I must first show how a substance analogous to my iodide of æthyle is formed, and then how by double decomposition with alcohol it produces æther. This is very easy; for sulphovinic acid is strictly analogous to iodide of æthyle plus iodide of hydrogen, which we should obtain by replacing SO^4 in its formula by an equivalent of iodine; and in order to represent the formation of this sulphovinic acid, which is well known to precede that of æther, the simplest mode is at the same time the one most free from hypothesis; it consists in stating the fact, that sulphuric acid and alcohol are transformed into sulphovinic acid and water, by half the hydrogen of the former changing places with the carburetted hydrogen of the latter: thus—



$$\frac{\begin{matrix}H\\H\end{matrix}SO^4}{\begin{matrix}C^2\,H^5\\H\end{matrix}O} = \frac{\begin{matrix}H\\C^2\,H^5\end{matrix}SO^4}{\begin{matrix}H\\H\end{matrix}O}$$

Now from this point it is clear that the process is the same as in the decompositions above described;

for by this sulphovinic acid coming in contact with an atom of alcohol, it reacts exactly in the same manner as the iodide did, forming of course sulphuric acid and æther :



$$\frac{\begin{matrix}H\\C^2H^5\end{matrix}SO^4}{\begin{matrix}H\\C^2H^5\end{matrix}O} = \frac{\begin{matrix}H\\H\end{matrix}SO^4}{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}O}$$

The sulphuric acid thus reproduced comes again in contact with alcohol, forming sulphovinic acid, which reacts as before ; and so the process goes on continuously, as found in practice.

We thus see that the formation of æther from alcohol is neither a process of simple separation, nor one of mere synthesis ; but that it consists in the substitution of one molecule for another, and is effected by double decomposition between two compounds. I therefore admit the contact theory, inasmuch as I acknowledge the circumstance of contact as a necessary *condition* of the reaction of the molecules upon one another. By reducing the formulæ of the alcohols to one atom of oxygen, I also retain the equality of volumes which the contact theory insists upon between the vapours of these bodies and their æthers, so that æther truly contains the elements of olefiant gas in addition to those of alcohol in one atom. But, on the other hand, I attach equal importance to all the essential facts of the chemical theory, and rest my explanation of the process as much upon them as upon those of the contact theory ; for, one-sixth of the hydrogen in alcohol truly exhibits different reactions from the remaining five, and must therefore be contained in that compound in a different manner from them ; and the alternate formation and decomposition of sulphovinic acid is to me, as to the partisans of the chemical theory, the key to explaining the process of ætherification.

Innovations in science frequently gain ground *only* by displacing the conceptions which preceded them, and which served more or less directly as their foundation; but, if the view which I have here presented be considered a step in our understanding of the subject, I must beg leave to disclaim for it the title of innovation; for my conclusion consists in establishing the connexion and showing the compatibility of views which have hitherto been considered contrary; and the best possible justification of the eminent philosophers who advocated either one of the two contending theories, is thus afforded by my reconciling their arguments with those of their equally illustrious opponents.

Before quitting the subject of ætherification, I would wish to add a few words on an application which naturally enough suggests itself of the fact to which the process is here ascribed. I refer to the transfer of homologous molecules in alternately opposite directions, which, as I have endeavoured to show, is the cause of the continuous action of sulphuric acid in this remarkable process. It may naturally be asked, why do hydrogen and carburetted hydrogen thus continuously change places? It cannot be from any such circumstance as superior affinity of one molecule over another, for one moment sees reversed with a new molecule the transfer effected during the preceding one. Now in reflecting upon this remarkable fact, it strikes the mind at once that the facility of interchange must be greater the more close the analogy between the molecules exchanged; that if hydrogen and amyle can replace one another in a compound, hydrogen and æthyle, which are more nearly allied in composition and properties, must be able to replace one another more easily in the same compound; and that the facility of interchange of hydrogen and methyle, which are still more similar, will be still greater. But if this be true, must not the exchange of one molecule for another of *identical* properties be the most easily effected of all? Surely it must, if there be any difference at all; and if so, the law of analogy forbids our imagining the fact to be peculiar to hydrogen among substances resembling it in other respects. We are thus forced to admit, that, in an aggregate of molecules of any compound, there is an exchange constantly going on between the elements which are contained in it. For instance, a drop of hydrochloric acid being supposed to be made up of a great number of molecules of the composition ClH, the proposition at which we have just arrived would lead us to believe that each atom of hydrogen does not remain quietly in juxtaposition with the atom of chlorine with which it first united, but, on the contrary, is constantly changing places with other atoms of hydrogen, or, what is the same thing, changing chlorine. Of course this change is not directly sensible to us, because one atom of hydrochloric acid is like another; but suppose we mix with the hydrochloric acid some sulphate of copper (of which the component atoms are undergoing a similar change of place), the basilous elements hydrogen and copper do not limit their change of place to the circle of the atoms with which they were at first combined, the hydrogen does not merely move from one atom of chlorine to another, but in its turn also replaces an atom of copper, forming chloride of copper and sulphuric acid. Thus it is, that at any moment of time in which we examine the mixture, the bases are divided between the acids; and in certain cases, where the difference of properties of the analogous molecules is very great, it is found that the stronger acid and stronger base remain almost entirely together, leaving the weaker ones combined. This is well known in the case of a mixture of sulphuric acid and borax, and is a confirmation of our fundamental assumption, that the greater the difference of properties, the more difficult is the alternate interchange of one molecule for another.

But suppose now that instead of sulphate of copper, we mixed sulphate of silver with our hydrochloric acid in aqueous solution, and that a similar division of the bases between the acids established itself in the first moment, forming four compounds, $SO^4 H^2$, $SO^4 Ag^2$, ClH, ClAg; it is clear that this last-mentioned compound, being insoluble in water, must, on its formation, separate out and remove from the circle of decompositions which solubility established. But of course the three compounds remaining in solution continue the exchange of their component parts, and give rise successively to new portions of chloride of silver, until as much of that compound is precipitated as the liquid contained equivalents of its component parts, a very small quantity remaining in solution and in the circle of decompositions.

Such is the general process of chemical decomposition. Of course a compound is removed as effectually from the circle of decompositions by possessing the gaseous form under the circumstances of the experiment, or even by being a liquid insoluble in the menstruum. I believe this explanation coincides in its second part with the one proposed many years ago by Berthollet; but not making use of the atomic hypothesis, upon which my explanation is based, that eminent philosopher went no farther back than the division of the acids between the bases on the mixture of salts, a fact which I have here deduced from the motion of atoms. It is well known that the general fact upon which Berthollet founded his view is denied by some eminent chemists of the present day ; but I believe the instances which they adduce are only apparent exceptions to the law, and will on further examination be found to afford additional confirmation of the truth of the great Savoysien's conception, as I have shown in the case of boracic and sulphuric acids.

In using the atomic theory, chemists have added to it of late years an unsafe, and, as I think, an unwarrantable hypothesis, namely that the atoms are in a state of rest. Now this hypothesis I discard, and reason upon the broader basis of atomic motion.

SUGGESTIONS FOR THE DYNAMICS OF CHEMISTRY DERIVED FROM THE THEORY OF ETHERIFICATION.*

THE human mind is only capable of understanding complicated phenomena when prepared by the study of simpler ones; and one of the most remarkable illustrations of this necessary order is afforded by the preparation of dynamical laws by the consideration of statical facts. In statics we consider phenomena in a state of rest, while in dynamics we study their change; and this distinction has been concisely stated by saying that the transition from the statical to the dynamical point of view, consists in superadding the consideration of *time* to that of space.

To represent the unknown cause of any change in phenomena, the word FORCE has been formed, and is generally retained until the law of that change has been discovered; so that the dynamics of a subject may be said to constitute the explanation of the phenomena belonging to it.

It unfortunately often occurs that names are mistaken for explanations, and people deceive themselves with the belief that, for instance, in attributing chemical decompositions to affinity, attraction, contact-force, catalysis, &c., they explain them.

But owing to the necessary dependence of investigations on our mental operations, there is always a deficiency of facts corresponding to the imperfection of theory ;—that is, we only seek and see those facts which are more or less connected with our theoretical notions, and in most cases shut our eyes to such cases as appear contrary to them. This is peculiarly the case with chemical theory and chemical facts at the present day; for our atomic theory represents only certain simple and definite proportions of combination, and our researches have been fruitful in the investigation of such cases alone, the number of compounds of which we know nothing being infinite, compared to those definite ones which we have studied.

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* [From *Notices of the Proceedings at the Meetings of the Members of the Royal Institution*, vol. i., 1851-1854, pp. 90-94.]

In fact, it is certain that if we could sufficiently disengage our minds from preconceived notions on the subject, we should view those substances, which, by more or less troublesome processes, we separate out from the bodies presented to us by nature, rather as exceptional and artificial products, than as the most normal and natural.

The lecturer submitted that the definite compounds hitherto exclusively acknowledged and studied by chemists, are in truth only exceptionally simple cases of combination, and that the consideration of chemists is only limited to them, because the atomic theory is as yet purely statical. The atomic theory has hitherto been tacitly connected with an unsafe and unjustifiable hypothesis, namely, that the atoms are in a state of rest ; the dynamics of chemistry will commence by the rejection of this supposition, and will study the degree and kind of motion which atoms possess, and reduce to this one fact the various phenomena of change, which are now attributed to occult forces. But although it will probably be generally used in connection with the atomic theory, the fact of motion is independent of any particulary theory; and however the properties of matter may be conceived, it will remain true, that a change of place among the representatives or possessors of these properties, is constantly going on, which produces the phenomena of chemical combination.

Chemical science has proved the indestructibility of matter, but it has yet to prove the indestructibility of motion or momentum by showing its transfer and dispersion among atoms.

There are many *primâ facie* evidences that *time* is necessary for chemical action:—but this fact, although it has been noticed, has not as yet entered into the explanation of phenomena.

The one instance in which a certain regular motion of the constituents of a mixture was first proved, is the process of etherification, of which the anomalous character has long since attracted the attention and study of many of the most eminent chemists, and has given rise to various theories which respectively represented part of the phenomena.

The lecturer referred to the importance of having a correct standard of comparison for the various chemical groups or molecules, and briefly alluded to the evidence afforded by the formation of the intermediate ethers, that alcohol and various bodies allied to it have of late years been incorrectly represented comparatively to metallic oxides and ethers, and that the weight of alcohol which is truly equivalent to ether or water, is not 46 but 23.

Having proved by a direct experiment that the formation of ether from alcohol is effected by substituting ethyle ($C_2 H_5$) for $\frac{1}{6}$ of the hydrogen of that body, the process of etherification by sulphuric acid was explained by a diagram, on which half the hydrogen in sulphuric acid was shown to change places with its analogue ethyle in alcohol ; and that the peculiarity of the process, *i.e.* its continuity, is owing to this change of place between hydrogen and ethyle, first taking place in one direction and then in the opposite; that is, that sulphuric acid becomes sulphovinic acid by taking up ethyle instead of an atom of hydrogen, and that it is then re-converted into sulphuric acid by resuming hydrogen instead of this ethyle, the first change forming water, the second ether.

By using successively two different alcohols, it was shown that the two steps of this decomposition can be separated and their reality proved. The process of etherification is thus effected by a succession of double decompositions, each of which considered individually is perfectly conformable to the law of definite proportions; but the alternation and continuous succession so clearly proved in them, is a fact unexplained by that law. A complete analogy between this process and the more familiar cases of chemical action is therefore only to be established by finding in these latter a similar atomic motion.

A little reflection is sufficient to show that such a motion actually exists. The fact of diffusion is in reality nothing but a change of place between atoms, effected by the mere action of the particles on one another; and there are many mechanical evidences of the communication of momentum from masses to atoms, and inversely.

It seems perhaps difficult to reconcile the apparent rest of the constituents of a mass with the existence of a continuous atomic motion; but there are many cases in which a rapid and continuous motion produces to our senses the appearance of a phenomenon at rest: thus, the rapid revolution of a white sphere produces the appearance of a circle at rest when seen in front, and that of an ellipse when viewed obliquely.

There are of course many points of view from which the motion of atoms may be considered; but it is inasmuch as it produces or facilitates decomposition, that the chemist has to regard it. We have in etherification an evidence of the tendency of atoms of analogous nature to change places continuously; and it is natural to suppose that the facility of this interchange must be greater in proportion to the analogy between the molecules, and greatest between like molecules. The lecturer expressed a confident hope that he would soon be able to give a direct experimental evidence of this conclusion, and proceeded to show how the admission of it explains, without the supposition of occult forces, the occurrence of double decompositions and the action of masses.

The exchange of analogous particles actually constitutes double decomposition; and its occurrence in alternately opposite directions causes the two substances used to alternate with the two other compounds formed by the exchange of their bases; so that in such a mixture, four substances are constantly to be found, the quantity of each substance corresponding to the average number of atoms which, in each moment of time, are in that state of combination.

Now it is clear that if an equal number of atoms of a hydrogen-salt, and of an iron-salt, reacting on one another, form a certain amount of the products of their double decomposition, a greater number of those products will be formed by doubling the quantity of the hydrogen-salt; for, the facility of interchange of iron with hydrogen remaining the same, the atoms of the iron-salt will then come more frequently in contact with those of the hydrogen-compound. Thus, on mixing a solution of sesquichloride of iron with sulphocyanide of hydrogen, a deep red colour gave evidence of the interchange of iron and hydrogen, forming sulphocyanide of iron and hydrochloric acid : but this exchange was not an operation effected once for all on the decomposing substances just coming in contact, but is constantly going on in the mixture ; and the quantity of the products of this interchange remains constant, because a similar double decomposition, equal in absolute number of atoms per unit of time, is constantly going on between these products, reproducing the original compounds. In evidence of this, the counterpart of the decomposition of sesquichloride of iron by hydrosulphocyanic acid was shown in the expulsion of this last acid by hydrochloric proved by the gradual diminution of the red colour on adding hydrochloric acid.

It is well known that caustic soda expels ammonia from its salts. But ammonia also expels soda : for it was shown, that a mixture of ammonia and hydrochlorate of soda dissolves less chloride of silver than the same quantity of ammonia alone ; and consequently, that a saturated solution of chloride of silver in aqueous ammonia is precipitated by dissolving chloride of sodium in it. The same occurs with the ammonio-sulphate of copper.

In conclusion, the lecturer referred to the question of the relative velocity of transfer of analogous atoms in opposite directions, which necessarily determines the proportion of the elements of two salts, contained in the form of their products of double decomposition, on these salts being mixed. On the mixture of equivalent proportions of a couple of salts in aqueous solution, a certain amount of decomposition ensues, forming two other salts, and the chemical force may be considered proportional to the quantity of one couple compared to that of the other. Now as the proportion is only kept up by the number of exchanges in the one direction being ABSOLUTELY the same in each moment of time as those in the opposite direction, it is clear that the relative velocity of interchange must be greatest between the elements of that couple of which the quantity is least; and chemical force must be inversely proportional to the velocity of these interchanges.

ON ETHERIFICATION.*

THE question of the transformation of alcohol into ether and water by the agency of sulphuric acid, may be divided into two parts; first, the relative weight of the substances engaged in the reaction; and, secondly, the actual process by which the transformation is effected. In a preceding memoir, read before the British Association last autumn, I briefly described the formation and properties of certain new ethers, which seemed to solve at least the first part of this question, *i. e.* the relative formulæ of alcohol and ether. I now lay before the Society a more exact account of the process by which these bodies were obtained, with their analysis, to which I have to add a direct evidence of the process by which sulphuric acid effects the decomposition of alcohol ; and, finally, I will describe a reaction with the acids of the adipic series, in which the formation of a peculiar series of bodies gives evidence that the formulæ of these acids should be halved similarly to those of the alcohols. But first, a few words on the previous views of the subject, as I understand them.

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* [From *The Quarterly Journal* of the Chemical Society of London, vol. iv. (1852), pp. 229-239.]

Of the relative formulæ of alcohol and ether, there have been especially two views ; one of which represented ether as the compound of olefiant gas with one atom of water, and alcohol as the compound of this same hydrocarbon with twice as much water ; the other considered ether as the oxide of a peculiar hydrocarbon $C_4 H_{10}$, and alcohol as the oxide of another hydrocarbon $C_2 H_6$. The first of these views was derived from a consideration of the analogy of the ethers with the salts of ammonia ; the second was formed rather from a comparison with metallic salts. To the French school, with Dumas at its head, we owe the former, and the great Berzelius suggested and advocated the latter. The study of the transformations of alcohol, and especially that by sulphuric acid, led to the modification of these views, and to the formation of others containing certain points of each ; and the most important of these is certainly the theory of Liebig, who, giving the name of ethyl to the hydrocarbon $C_4 H_{10}$, represented ether as its oxide, and alcohol as the hydrate of that oxide. From novel and highly important considerations, Gerhardt arrived at the formulæ of Berzelius, and compared alcohol in its reactions to an acid. The process of etherification, of which the continuous nature had been discovered by Boullay, was, from the different points of view afforded by the above-mentioned formulæ, of course represented differently. Berzelius and the contact-school, seeing in ether a more complex atom than alcohol, and considering the apparently indefinite action of sulphuric acid, were especially struck with the difference between etherification and other cases of chemical action, and supposed some different force must be active in it, which was christened *catalysis*. It was certainly an important step towards the philosophical solution of the question, which Liebig made, in urging the resemblance to chemical action, and explaining more successfully than Hennel had been able to do, the process by chemical affinity, overcome successively by the decomposition of sulphovinic acid by heat. The mutual action of these various theories had exercised a decomposing influence upon them all, and the elegant experiments by which Graham shewed the untenable nature of the chemical theory, afford conclusive evidence of that decomposition. Now I submit that the theory here laid before you, with its experimental conclusions, combines the requisitions of the several parties in this great discussion, and may be considered as closing it amicably, by shewing that each point of view contained part, and an important part, of the facts. The explanation of the process is composed of two parts—first, proving in etherification the occurrence of decompositions strictly analogous to common phenomena usually attributed to chemical affinity, and as explicable by such a name as those phenomena may be; and, secondly, on finding that over and above the commonly observed phenomena of chemical action, there occurs in this process a new circumstance, it will be necessary to prove the occurrence of this circumstance in the more familiar cases.

Formation of ether by double decomposition.—In the paper above referred to, I stated the fact of this reaction, which consists in the elimination by metallic sodium of the hydrogen in alcohol, which has to be replaced by ethyle, and the action of the iodide of ethyle on the compound thus formed, which, from its analogy with the hydrate of potash, I will call *ethylate of potash.** It is important that the alcohol used in this and all similar reactions be as anhydrous as possible ; and the naphtha which surrounds the sodium must be removed completely by drying with bibulous paper and immersion for a few seconds in a small·portion of absolute alcohol, which serves successively to rinse all the pieces of metal used in one experiment. The pieces of sodium thus purified are thrown, one at a time, into the alcohol which is to be transformed into ether, until the liquid is completely saturated with them ; after cooling, it is treated with iodide of ethyle, and distilled, the ether passing over with alcohol vapour and some of the iodide. To remove these admixtures, the distillate should be treated with sodium, which, as long as alcohol is present in equivalent quantity with the iodide, forms more ether, and when all the iodide has been thus decomposed, forms with the remaining alcohol, ethylate of sodium, from which the ether may be distilled off in a state of perfect purity. Prepared in this manner, ether is identical in its boiling-point and all its properties with that prepared by the action of sulphuric acid.

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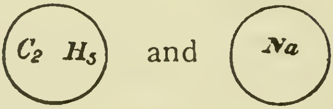
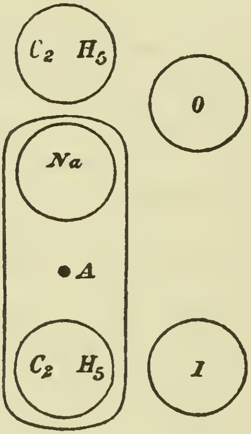
* The atomic weight of hydrogen and the metals, iodine, &c., is in this paper according to Laurent and Gerhardt's notation, assumed at half their equivalents. The compound radicals methyle (CH_3), ethyle (C_2H_5), amyle (C_5H_{11}) are of course reduced to the same unit.

The reaction is easily understood by the following diagram, in which the atoms are supposed to be capable of changing places by turning round upon the central point A.





It is clear that we thus get $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}O$ and Na I. The circles are merely used to separate off the atoms or units of comparison. To express the corresponding decomposition of iodide of ethyle by hydrate of potash, forming alcohol, we should replace the ethyle of the sodium-compound by hydrogen, and the same change of place between sodium and ethyle forms $\begin{matrix}H\\C_2H_5\end{matrix}O$ (alcohol) and Na I.

Three-carbon ether, Ethylate of methyle, or Methylate of ethyle.—This compound may be prepared by the action of iodide of ethyle on the methylate of sodium, $\begin{matrix}CH_3\\Na\end{matrix}O$, or inversely, by acting on ethylate of sodium by iodide of methyle. Of these two processes, I however prefer the former, from the fact of iodide of ethyle boiling at so much higher a temperature than the ether, that any excess of it is easily separated by distillation. This ether is purified in the same manner as the preceding one. On account of its more powerful action, I generally preferred potassium to sodium for the removal of the last traces of alcohol from an ether; and in order that the action of the metal might be complete, the distilling apparatus was so arranged that the distillate constantly flowed down into the retort until the action had completely ceased, and then only was the ether distilled over from the fixed products of that action. The boiling-point of this ether is 11° C., and it was therefore usually distilled simply by removing from the retort the frigorific mixture by which it was retained in the liquid state. In order to effect its combustion, a small quantity was introduced into a strong bulb at the extremity of a piece of thermometer tubing, about 6 inches long, which had been previously weighed, and which being bent at a right angle, could be fixed by means of a cork into the end of a combustion-tube, open at both ends, and was in the power of the operator.

By this process, the ether being burnt by oxide of copper, the following results were obtained:

0.2215 grm. of liquid gave:
0.482 ,, ,, carbonic acid, and
0.2685 ,, ,, water.

The percentage composition as deduced from this, is:

	By Experiment.	By Calculation.	Difference.
Carbon . . .	59.39	60.00	0.61 –
Hydrogen . .	13.46	13.33	0.13 +
Oxygen . . .	27.15	26.67	0.48 +

The density of its vapour was found to be :

By Experiment.	By Calculation.	Difference.
2.158	2.084	.074

Weight of globe and air at 12° C. and 30.05 in. bar. . . . . . = 53.6240 grms.
Weight of globe and vapour, the temp. at moment of sealing the point 23°.5 C., and bar. 30.05. . . . . = 54.1790 ,,
Capacity of globe . . . . = 438 cub. centi.
Residual air at 16° C. and 30.05 bar. . = 23 ,,

Hence its formula is $\begin{matrix}C_2H_5\\C\,H_3\end{matrix}O$, or empirically C_8H_8O.

Now it being thus established beyond doubt that this substance contains 1 volume ethyle, 1 vol. methyle, with 1 vol. oxygen, the three condensed into two volumes, and the two opposite modes of preparing it proving that the two atoms of hydrocarbon are contained in *like* manner in it, we may view it either as the ethylate of methyle, *i. e.* alcohol in which one atom of hydrogen is replaced by methyle, or else as methylate of ethyle. I am, however, convinced that the simplest view that can be formed of its constitution is to be gathered from a comparison with water, from which it may be produced by replacing one atom of hydrogen by ethyle and the other by methyle.

Seven-carbon ether, *Amylate of ethyle*, or *Ethylate of amyle.*—This ether is one of the most easily prepared of these peculiar bodies, and is perfectly identical when prepared from amylic alcohol and iodide of ethyle, or ethylic alcohol and iodide of amyle. I have prepared it in considerable quantity by each process, and could discover in no respect any difference of properties between the products ; its boiling-point is 112° C. Combustion performed with oxide of copper.

0.2350 grm. yielded :
0.624 „ of carbonic acid, and
0.276 „ of water ;

or in 100 parts.

	Experiment.	Calculation.	Difference.
Carbon . . .	72.42	72.41	0.01 +
Hydrogen . .	13.99	13.79	0.20 +
Oxygen . . .	13.59	13.80	0.21 −

Its formula is therefore $\begin{matrix}C_2H_5\\C_5H_{11}\end{matrix}O$, or empirically $C_7H_{16}O$.

The density of its vapour was found to be :

By Experiment.	Calculation.	Difference.
4.042	4.031	0.011

Weight of globe and air at 11° C., bar. at 29.60 in. . . . . . = 93.7790 grms.
Weight of globe and vapour, the temp. at moment of sealing being 135.5° C., and bar. 29.64 . . . . = 94.6755 „
Capacity of globe . . . . = 377 cub. centi.
Residual air at 25° C., and 29.60 bar. . = 3 „
Increased expansion of glass globe at 135° C. . . . . . . = 0.92 „

Six-carbon ether.—Boils at 92° C.; analysis as follows:

0.2050 grm. of liquid gave as the produce of combustion :
0.528 „ „ carbonic acid, and
0.256 „ „ water ;

which gives in 100 parts :

	Experiment.	Calculation.	Difference.
Carbon . .	70.244	70.588	0.344 −
Hydrogen .	13.873	13.725	0.148 +
Oxygen . .	15.883	15.686	0.197 +

Hence the formula $C_6H_{14}O$.

The density of its vapour was found to be:

By Calculation.	By Experiment.
3·546	3·75

Weight of globe and air, temp. 10° C., bar. 29.72 in. . . . . . = 90.689 grms.
Weight of globe and vapour temp. at moment of sealing the point 110° C., and bar. 29.72 in. . . . . = 91·553 ,,
Capacity of globe . . . . = 407 cub. cen.
Residual air at 19½° C., and 29.93 inches bar. . . . . . = 10.75 ,,

A second experiment gave nearly analogous results:

Weight of globe and air, temp. 11.5° C., bar. 30 in. . . . . = 85.0855 grms.
Weight of globe and vapour, temp. at moment of sealing, 111.5° C., bar. 30 in. . . . . . . = 85.8925 ,,
Capacity of globe . . . . = 377 cub. centi.
Residual air at 22° C., and 30 in. bar. = 4·5 ,,

Calculated density from this latter experiment = 3.73.

In my former paper, I showed how the formation of these intermediate ethers proves the atomic weight of the alcohols to be half that which they have of late years been considered, so that their equivalent occupies in the state of vapour the same volume as that of ether, water, &c. It is of course only a *relation* which I here establish, and if any chemists prefer doubling the present formulæ of ether, water, and all the metallic oxides, they will accomplish the same object in an unnecessarily clumsy manner. But the same arguments which require me to halve the atomic weight of alcohol must of course apply to its compounds, and sulphovinic acid, which is nothing else than the sulphate of alcohol, as represented by the formula $\genfrac{}{}{0pt}{}{\AE}{H}SO_4$; and the process of etherification is at once explained; for by the reaction of this sulphovinic acid upon alcohol, we have at once ether and sulphuric acid, which again reacts upon the atoms of alcohol, forming with the first, $\genfrac{}{}{0pt}{}{\AE}{H}SO_4$ and $\genfrac{}{}{0pt}{}{H}{H}O$, and with the second $\genfrac{}{}{0pt}{}{\AE}{\AE}O$ and $\genfrac{}{}{0pt}{}{H}{H}SO_4$. Thus it is that the sulphovinic acid formed at the end of a long process of etherification is not the same as that which formed at first, but being perfectly like, it cannot of course be distinguished from it. To prove this point, I made sulphuric acid react successively upon two alcohols, so that it took the hydrocarbon from the first, and gave it up to the second, forming an intermediate ether, and finding only the second alcohol to react upon, remained at last combined with its hydrocarbon alone. The experiment was performed in the following manner: Sulphamylic acid was prepared by the action of sulphuric acid upon its equivalent weight of fusel oil, and this compound was treated with vinic alcohol by the continuous process, until the distillate consisted of pure 4-carbon ether. The residue was then examined, and found to contain *no* sulphamylic acid, but only sulphovinic, the 7-carbon ether being easily separated out from the first portions of the volatile product. I next tried the action of sulphuric acid upon a mixture of equivalent weights of the two alcohols, expecting similarly to have the production of the 7-carbon ether, and the result fully justified my expectations; for on treating the mixture by the continuous process, a distillate was obtained consisting of two liquids, water and a light ethereal liquid, which, after two distillations over fused potash, was distilled with the thermometer, and rose from 40° to 180°. A considerable portion was separated by repeated distillation at the temperature of 112° C. I shewed by combustion the exact composition of the 7-carbon ether.

0.25075 grm. of ether yielded :
0.6665 „ „ carbonic acid, and
0.3100 „ „ water ;

which gives the following percentage :

	Experiment.	Calculation.	Difference.
Carbon . . .	72.46	72.41	0.05 +
Hydrogen . .	13.73	13.79	0.06 −
Oxygen . . .	13.81	13.80	0.01 +

The last portions of the distillates were added together and re-distilled, their temperature rising rapidly to 176°, where it remained stationary for some time, and the liquid which came over at this temperature shewed the composition of amylic ether. Thus :

0.2045 grm. of distillate produced :
0.5685 „ „ carbonic acid, and
0.2595 „ „ water,

giving the following percentage composition :

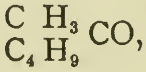
	Experiment.	Calculation.	Difference.
Carbon . . .	75.81	75.95	0.14 −
Hydrogen . .	14.09	13.92	0.17 +
Oxygen . . .	10.10	10.13	0.03 −

The smell of common ether was very perceptible in the first portions of the mixture which came over. It is thus clear that by the action of sulphuric acid on the mixed alcohols, three ethers are formed by the reaction of sulphovinic and sulphamylic acids on each of the alcohols respectively. On treating in a similar manner a mixture of equivalent parts of methylic and amylic alcohols, a corresponding result was obtained, the products being, however, more easily separated than in the preceding instance, owing to the greater difference of their boiling-points. The experiment was performed in the following manner: 17 oz. of aqueous methylic alcohol was mixed with 38 oz. of fusel oil, which had been ascertained by a previous trial to contain the equivalent quantity of amylic alcohol; 7 oz. of this mixture were added to 5 oz. of sulphuric acid, and heated to 120°, at which temperature the etherification commenced; the mixed alcohols were allowed to run into the retort, so as to maintain the level of the liquid in it a little higher than it had been at first, and in this manner the whole of the mixture was converted into a colourless distillate, composed of about one volume of water to three of the mixed ethers, and possessing a faint smell of sulphurous acid. The theory of the purification of this mixture by distillation over dry hydrate of potash, is easily intelligible from the fact that that substance becomes transformed in contact with alcohol into ethylate of potash, with formation of water; and similarly into amylate of potash by the action of amylic alcohol. Thus it is that the whole of these alcohols are kept back by the potash, and the excess of it even takes up pretty completely the water, so that the mixture of ethers, after this treatment, is scarcely acted on at all by potassium. We have in these reactions the best evidence of the nature of the action of sulphuric acid in forming common ether, or in accelerating the formation of the so-called compound ethers; for acetic ether is formed from acetic acid, just as ethylic ether from alcohol, by the replacement of hydrogen by ethyle. And if the circumstance of containing hydrogen, which is replaceable by other metals or radicals, be the definition of an acid, we must consider alcohol as acting the part of an acid in these reactions. Common ether is its ethyle-salt, the 3-carbon ether is its methyle-salt, and so on, just as the potassium-alcohol or ethylate of potash is its potassium-salt.

But before proceeding further in the investigation of these circumstances, I must beg leave to direct your attention for a moment to the relation between alcohol and acetic acid, and show how the conclusions just arrived at concerning the former will be applicable to the atomic weight of the latter. You are aware that this acid is essentially monobasic in its characters, like the other terms of the series to which it belongs, and that, in conjunction with other reasons, this circumstance has been urged by M. Gerhardt as a ground for halving its formula. Now as acetic acid is formed from alcohol by replacing one-third of its hydrogen by oxygen, there are strong grounds for assuming a similar atomic constitution in both, and of writing acetic acid at half its usual atomic weight, in accordance with the reduced formula of alcohol. Viewing, therefore, alcohol as water in which half the hydrogen is replaced by ethyle, $\begin{matrix}C_2H_5\\H\end{matrix}O$, we shall consider acetic acid as containing one equivalent of oxygen in the place of two atoms of hydrogen of that radical, or $\begin{matrix}C_2H_3O\\H\end{matrix}O$. Organic chemistry is replete with instances of differences similar to those between alcohol and acetic acid, and produced by the substitution of an electro-negative element for hydrogen; take for example phenylic alcohol, a feeble acid, in which the substitution of hyponitric acid for hydrogen produces stronger and stronger acids up to carbazotic, a very strong acid ; or again, consider the diminution of the alkaline properties of aniline by the substitution of more and more chlorine for its hydrogen, until they entirely disappear in the trichloraniline, as shewn by Dr. Hofmann. Now we actually prepare acetic acid by the action of oxygen upon alcohol under certain circumstances, and observe a double decomposition perfectly analogous to that produced by chlorine in its action on hydrocarbons, water being formed, and the hydrogen thus taken out being replaced by oxygen ; but it is clearly not the basic atom of hydrogen in alcohol which is thus replaced, for acetic acid retains it with its characteristic properties heightened. It is, therefore, the hydrogen of the radical which is thus replaced by oxygen, and acetic acid differs from alcohol by containing, instead of ethyle, this other radical, differing from it by having oxygen in lieu of an equivalent of hydrogen, and which may be called *oxygen-ethyle*, or *othyle*. We are thus led to consider the atom of ethyle as containing half the number of atoms which are generally ascribed to it, and as occupying in the state of vapour two volumes and not four. But I endeavoured to obtain an experimental evidence of the correctness of this conclusion, and sought it in the decomposition of the acetates by heat, by which their elements separate into acetone and carbonate. In this decomposition, the process differs according to the two views of the constitution of acetic acid ; if the atom of acetate of potash be $C_4\begin{matrix}H_6\\K_2\end{matrix}O_4$, acetone and carbonate are formed by the division of one atom ; whereas, if the formula of the acetate be $C_2\begin{matrix}H_3\\K\end{matrix}O_2$, the reaction consists in a double decomposition, by which CH_3 in one atom is replaced by KO, *i. e.* methyl by peroxide of potassium, or C_2H_3O replaced by CKO_2. To ascertain which of these two opposite views is the more correct, I dissolved in water equivalent weights of acetate of soda and valerate of potash, and evaporated rapidly to dryness. The mixed salts were introduced into a retort, and subjected to dry distillation, the oily distillate shaken with aqueous potash, to remove the acids which might have come over undecomposed, and after separation from the potash, distilled with the thermometer. By uniting the products of repeated distillations, a liquid was obtained, boiling with perfect regularity at 120° C., and constituting nearly two-thirds of the original distillate. This body was found to possess the composition $C_6H_{12}O$, as shewn by the following combustion with oxide of copper.

0.704 grm. of carbonic acid and 0.2935 grm. of water were the results of the decomposition of 0.2690 grm. of the liquid; the percentage relations, as obtained by experiment and calculation, are as follows:

	Experiment.	Calculation.	Difference.
Carbon . . .	71.38	72.00	0.62 –
Hydrogen . .	12.12	12.00	0.12 +
Oxygen . . .	16.50	16.00	0.50 +

Hence the formula is,  $\begin{matrix}C\ H_3\\C_4\,H_9\end{matrix}CO$, or empirically $C_6H_{12}O$.

The same experiment was performed with various other terms of the series, and similar results obtained, the details of which I will communicate on a future occasion. On distilling equivalent parts of an acetate and formiate, the corresponding reaction would consist in the formation of a body having the composition of aldehyde, which is the hydruret of ethyle, as acetone is its methyle-compound.

The method here employed of stating the rational constitution of bodies by comparison with water, seems to me to be susceptible of great extension ; and I have no hesitation in saying that its introduction will be of service in simplifying our ideas, by establishing a uniform standard of comparison by which bodies may be judged of.

ON THE CONSTITUTION OF SALTS.*

CHEMISTS have of late years considerably extended the meaning of the term salt ; acids and bases are now rather viewed as acid salts and basic salts respectively, than as compounds of fundamentally different arrangement, and there seems reason to believe that the molecular structure of the so-called simple bodies is analogous to that of salts. Thus any view which best explains the properties of salts may be expected to apply ultimately to the molecular structure of matter in general.

It was remarked that a serious error had crept into chemical science by the introduction of a different unit of comparison in organic chemistry to that which is employed in the inorganic department of the science.

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* [From *Report of the Twenty-first Meeting of the British Association for the Advancement of Science*, 1851, part 2, p. 54.]

The removal of this error and adoption of an uniform standard of comparison, naturally leads to viewing chemical action as consisting in substitutions rather than in direct combinations. The best studied processes of organic chemistry have been found to consist of double decompositions. Numerous other instances were mentioned, in which the result may be far more simply explained by a process of double decomposition than by the supposition of unknown predisposing affinities invented for each; and various arguments were adduced why the same mode of reasoning ought to be extended even to the simplest phænomena of inorganic action generally considered as mere combinations or separations. It was shown that water may be assumed as a very general if not universal type and standard of comparison, by viewing other bodies as formed from it by the replacement of one or more atoms of hydrogen in water by their equivalent of various simple or compound radicals. The atom of radical thus replacing hydrogen is sometimes equivalent to one atom of that element; in other cases it is equivalent to two. The difference between monobasic acids, such as nitric and bibasic acids as sulphuric, were shown to follow as a necessary consequence of such a difference of the respective radicals NO_2 and SO_2.

ON THE CONSTITUTION OF SALTS.*

THERE is strong reason for believing that all questions concerning the chemical constitution of matter will be most tangible when considered from the point of view of the constitution of salts, which are the groups whose arrangement and transformations are most susceptible of being ascertained experimentally. The elementary bodies themselves have been now shown † to obey a certain force of combination between their particles, analogous though generally inferior to that which holds together the constituents of a salt ; and any general conclusions which may be established for salts, will therefore extend to them. Now, to have clear and connected notions of any order of phænomena, it is necessary to be able to judge of the various cases belonging to it from the same point of view ; or, in other words, to have a uniform standard of comparison. Thus if the value of mechanical forces had to be compared, it would evidently not do to measure the one in pounds and the other in kilogrammes, unless the relative value of these units were known, *i. e.* unless the statement made in the one could be reduced to its equivalent in the other. Such unity has as yet been but little attended to by the majority of chemists ; and the different branches of the science remaining disconnected, their efforts were directed to establish details rather than general laws. Thanks to the numerous facts which have been thus established, it is now possible, and even necessary, to do something more. The researches of MM. Laurent and Gerhardt have been mainly directed to this point, and it is well known how fruitful their conclusions have already proved. The following remarks have an intimate connexion with those conclusions, and will hardly be intelligible without a knowledge of them.

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* [From *The Chemical Gazette*, vol. ix. (1851), pp. 334-339.]

† See Mr Brodie's research "On the Condition of certain Elements at the moment of Chemical Change."

We are all agreed that chemistry is concerned with the material process of the transformations and changes which matter undergoes, and that the study of the properties of matter in themselves, as long as they undergo no change, belongs to physics. The chemical formulæ, by which we describe more briefly than by words the transformations supposed or known to take place, have as yet answered that purpose very imperfectly, and have presented great irregularity of method; for although generally denoting a certain arrangement of atoms, or at least certain differences of arrangement, they are sometimes used to describe the origin of a compound or its decompositions, without forming any other representation of its actual constitution than what may be contained in such a statement. M. Gerhardt has, in a recent memoir published conjointly with M. Chancel, given considerable development to this latter method; and his so-called synoptic formulæ will, I think, be found very suggestive and useful expressions. But formulæ may be used in an entirely different, and yet perfectly definite manner, and the use of two distinct points of view will perhaps not be unserviceable. They may be used as an actual image of what we rationally suppose to be the arrangement of constituent atoms in a compound, as an orrery is an image of what we conclude to be the arrangement of our planetary system ; and decompositions may be actually effected between them by the exchange of a molecule in one group for a molecule in another. Gerhardt's formula for sulphate of soda (if he extends his principles to inorganic chemistry) would be sulphuric acid plus soda minus water. This, no doubt, gives a possible origin of the salt, but by no means a possible decomposition ; in other instances the inverse would be the case. But the term sulphate of soda does not mean a body formed in any one particular way ; it is equally applicable to the product of the action of sulphuric acid on chloride of sodium, or on carbonate of soda, or even to the product of the action of soda on sulphate of iron. The written name should be made to represent what we conceive a compound *to be*, and should be such that it might be formed by any one of the various processes by which the compound may be prepared. Sulphate of soda is a physical term, and corresponds to purely physical properties ; for the substance subscribed by it does not by itself undergo any change, but only when acted upon by certain foreign substances under suitable circumstances.

When we study a molecule by itself, we study it physically ; chemistry considers the *change* effected by its reaction upon another molecule, and has to describe the process by which that change is effected. A chemical decomposition should therefore be represented by the juxtaposition of the formulæ of the reacting substances, and by effecting in these formulæ the change which takes place in the mixture.

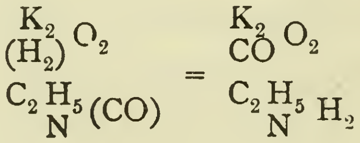
The adoption of such a method will of course necessitate the adoption of types, from which, by the replacement of certain elements or molecules, we can deduce the constitution of more and more complex groups. I believe that throughout inorganic chemistry, and for the best-known organic compounds, one single type will be found sufficient; it is that of water, represented as containing 2 atoms of hydrogen to 1 of oxygen, thus $\genfrac{}{}{0pt}{}{H}{H}O$. In many cases a multiple of this formula must be used, and we shall presently see how we thereby get an explanation of the difference between monobasic and bibasic acids, &c.

I will here give a few examples of the application of this universal type to the formulæ of common substances. The experiments of M. Chancel, agreeing in result with my own, have clearly proved that the numerous family designated as hydrated oxides are not formed by the juxtaposition of an atom of water with an atom of metallic oxide, *e. g.* $K_2O + H_2O$, but that the equivalent of the molecule is half of that quantity, namely $\genfrac{}{}{0pt}{}{H}{K}O$; they are not compounds of water, but products of substitution in water. This fact is as applicable to the compound as to the simple radicals; and alcohols, which are truly hydrated oxides, must be considered as products of substitution of the compound radicals, methyle, CH_3; æthyle, C_2H_5; amyle, C_5H_{11}; œnanthyle, C_7H_{15} (Buis), &c., for half the hydrogen of water, $\genfrac{}{}{0pt}{}{H}{(CH_3)}O$, $\genfrac{}{}{0pt}{}{H}{C_2H_5}O$, &c. The anhydrous oxides of metals have both atoms of hydrogen replaced by the metal, as $\genfrac{}{}{0pt}{}{K}{K}O$, in the same way as common æther and its homologues have æthyle in place of both the atoms of hydrogen.

In extending this mode of notation to salts and compound æthers, we must of course keep carefully in view the capacity of saturation of their acids, writing the monobasic acids as hydrochloric, nitric, acetic, &c., at half their usual equivalents, ClH, NO_3H, $C_2H_4O_2$, but retaining the customary atomic weights of the bibasic acids, as sulphuric, carbonic, oxalic, &c.

As alcohol is truly an acid in its reaction, we must of course consider the potassium-alcohol, $\begin{matrix}C_2H_5\\K\end{matrix}O$, as its salt, though alkaline in its reactions. We only need to replace 2 atoms of hydrogen in the radical of this salt by oxygen, to have a compound of which the saline character is acknowledged, acetate of potash, $\begin{matrix}(C_2H_3O)\\K\end{matrix}O$. The most simple manner of representing the rational constitution of this compound is to state that it contains, in lieu of the æthyle of the former salt, an oxygen-æthyle, C_2H_3O, which we may term othyle. If the 2 atoms of hydrogen in water were replaced by this othyle, we should have anhydrous acetic acid, $\begin{matrix}(C_2H_3O)\\(C_2H_3O)\end{matrix}O$. In fact, the so-called anhydrous acids are nothing else than the *æthers* of the hydrated acids.

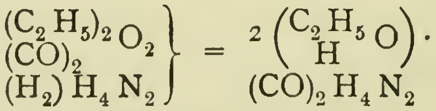
Again, by replacing the potassium in the æthylate, $\begin{matrix}C_2H_5\\K\end{matrix}O$, by its equivalent of cyanogen (which may be effected by the action of iodide of cyanogen), we obtain a compound of the composition $\begin{matrix}C_2H_5\\(NC)\end{matrix}O$, that is, cyanic æther. It is well known, from Wurtz's elegant researches, that by acting upon this body by hydrate of potash, we obtain carbonate of potash and æthylamine; that is, in the place of carbonic oxide in the cyanate, we get hydrogen, and reciprocally with the hydrate. Now can this exchange be represented more simply than by stating the fact, that, in the following diagram, the hydrogen of the 2 atoms of hydrate of potash changes places with the carbonic oxide of the cyanate :—



$$\begin{array}{l}\begin{matrix}K_2\\(H_2)\end{matrix}O_2\\ \begin{matrix}C_2H_5\\N\end{matrix}(CO)\end{array} = \begin{array}{l}\begin{matrix}K_2\\CO\end{matrix}O_2\\ \begin{matrix}C_2H_5\\N\end{matrix}H_2\end{array}$$

1 atom of carbonic oxide is here equivalent to 2 atoms of hydrogen, and by replacing them, holds together the 2 atoms of hydrate in which they were contained, thus necessarily forming a bibasic compound, $\begin{matrix}(CO)\\K_2\end{matrix}O_2$.

If we knew how to form the compound COCl, *i. e.* phosgen, with half as much chlorine, it would be easy, by the reaction of it upon our æthylate of potassium, to prepare oxalic æther (and chloride of potassium). Oxalic æther is therefore alcohol in which the basic hydrogen is replaced by carbonic oxide with twice the equivalent that it possesses in the carbonates ; and the best evidence of the truth of this view is afforded by M. Dumas's elegant reaction of ammonia upon the æther, forming the compound of amidogen with carbonic oxide (oxamide), and replacing the carbonic oxide by hydrogen, *reproducing alcohol* :—



$$\left.\begin{array}{l}\begin{matrix}(C_2H_5)_2\\(CO)_2\end{matrix}O_2\\(H_2)H_4N_2\end{array}\right\} = \begin{array}{l}2\left(\begin{matrix}C_2H_5\\H\end{matrix}O\right).\\(CO)_2H_4N_2\end{array}$$

Sulphurous acid is another radical capable of replacing hydrogen ; and the sulphates are thus reduced to our type, being bibasic for the same reason as the carbonates. We have thus for sulphuric acid, $\begin{matrix}SO_2\\H_2\end{matrix}O_2$;

acid sulphate of potash, $\begin{matrix}SO_2\\HK\end{matrix}O_2$; neutral sulphate, $\begin{matrix}SO_2\\K_2\end{matrix}O_2$, &c.

There are various reactions, both of formation and decomposition, of sulphates, which bear out this view; for instance, chlorosulphuric acid, SO_2Cl_2, in contact with 2 atoms of water, at once replaces half the hydrogen in both by SO_2, forming 2 (ClH) and $\begin{matrix}SO_2\\H_2\end{matrix}O_2$. And again, the difference of the action of zinc upon sulphuric acid according to the concentration, evolving at one time hydrogen, at another sulphurous acid, affords evidence that the sulphurous acid is contained in a manner similar to the hydrogen.

Nitric acid presents, according to the usual view of its constitution, a singular difference between its behaviour to organic and to inorganic compounds; but this difference is owing merely to the error of that view. We are taught that nitric acid combines directly with mineral bases; but when reacting upon hydrogen compounds, it has a powerful tendency to replace hydrogen by hyponitric acid. Now if hydrogen, in organic compounds without number, be replaceable by hyponitric acid, why should not also the hydrogen in hydrate of potash be so replaceable? The product of that substitution would be no very improbable body, only common nitrate of potash, $\begin{matrix}(NO_2)\\K\end{matrix}O$.

One more example, and I have done. Chlorine is well known to react upon hydrogen-compounds by replacing hydrogen by chlorine, with formation of hydrochloric acid. So it is also when it reacts upon water in presence of bases, $\begin{matrix}Cl\\H\end{matrix}O$ (hydrated hypochlorous acid), and ClH being formed. In like manner we have, for the series of oxygen acids of this radical, the formulæ $\left.\begin{matrix}\mathrm{ClO}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}$, chlorous acid ; $\left.\begin{matrix}\mathrm{ClO_2}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}$, chloric acid ; $\left.\begin{matrix}\mathrm{ClO_3}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}$, perchloric acid.

In order to accomplish what I above alluded to as a desideratum for the explanation of chemical reactions, namely effecting between the formulæ of the reagents the interchange supposed to take place in the mixture, I have fixed the symbols of those atoms which have to change places upon the extremities of a piece of card, so fixed by a pivot to the board that by turning round 180° it reverses the positions of the exchanging atoms.

I would not have brought before the public considerations so purely theoretical as the above, had I not found the conclusions of considerable practical utility in the study of reactions.

In the theory of types, we owe to M. Dumas an idea which has already been the vehicle of many an important discovery in science, and which is undoubtedly destined to receive still more general application.

To prevent misunderstandings, it may be as well to state, that the radicals which I have here so freely used are not supposed to be in their compounds absolutely the same as in the free state. The same remark applies with equal force to metallic bodies, which on entering into combination give off a certain amount of heat, and thus assume different properties. To say that metallic zinc is contained in its sulphate is an expression authorized by usage, but is only strictly true by abstraction from most of the properties of the metal. The material atom, which under certain circumstances possesses the properties which we describe by the word "zinc," is no doubt contained in the sulphate, but with different properties, and in the chloride with properties different from either; so also of the compound radicals.

It is to be hoped that we may soon be able to give an account of the nature of the processes by which these changes of properties are effected; but that task can only be entered upon when we have obtained exact determinations of the relative momentum of atoms in various compounds, the proportion of which to their masses determines their physical and chemical properties.

ON GERHARDT'S DISCOVERY OF ANHYDROUS ORGANIC ACIDS.*

THE discovery by M. Gerhardt of a number of anhydrous organic acids has thrown so much light on one of the most important questions of chemical philosophy, that it constitutes one of the most remarkable illustrations of the manner in which the rich materials of organic chemistry may be brought to bear on the explanation of the phenomena of chemical action and the laws of chemical combination.

It is not unworthy of remark, that the bodies prepared by Gerhardt had for some years past been supposed to exist ready formed in combination with water and other bases, and that the chief objection to that supposition was founded on the circumstance of their never having been separated from such combination, and presented in an isolated form. In fact Gerhardt has supplied the very link in the chain, which was expected to constitute evidence for a familiar theory of the constitution of salts. But the process by which the result was attained is even more important than the result itself, and has led to our drawing from that result a conclusion different from that which was generally expected. Chemistry aims at discovering the nature of that action by which substances of opposite properties undergo those remarkable changes which we call chemical combination ; and it naturally follows from this view of its objects, that chemical science is more advanced by the discovery of a new *process* than by the discovery of a new *substance ;* and its theories are more immediately affected by the nature of a process of change than by any physical fact, such as the existence of a peculiar body or class of bodies. Thus it is that the method of isolating the anhydrous organic acids, has afforded evidence of a new view of the constitution of acids and salts.

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* [From *Notices of the Proceedings at the Meetings of the Members of the Royal Institution*, vol. i., 1851-1854, pp. 239-242.]

A few words may serve to give an idea of the previous state of the question.

Compounds of oxygen-acids were supposed to consist of the anhydrous acid united with an oxide. Thus hydrated sulphuric acid was represented as containing the anhydrous group SO_3 plus an atom of water H_2O ; and in the saturation of this hydrated acid by a base such as potash, it was conceived that this oxide replaced the water. The existence of anhydrous sulphuric acid in an isolated state, and the fact that it so readily combines with water, was urged as an argument in favour of this theory ; and the same holds good with phosphoric, carbonic, sulphurous, lactic, nitrous, and even (according to the recent discovery of Dessaignes) nitric acid.

However simple this view might appear and however satisfactory it might be in explaining those cases of combination for which it was specially intended, chemists soon became acquainted with bodies perfectly analogous in their general properties to the oxygen-acids, and producing by their action upon bases similar effects, but which, from the fact of their containing no oxygen, could not possibly be conceived as made up of water and an anhydrous-acid. For instance, hydrochloric acid was proved, both analytically and synthetically, to be composed of nothing but chlorine and hydrogen ; and when it combines with potash, the hydrogen is found to leave the chlorine, whilst potassium takes its place.

Being desirous of simplifying as far as possible their views of these phenomena, and of extending the same explanation to all like cases, certain chemists were led to imagine a new mode of representing the constitution and reactions of oxygen-acids, which had the advantage of connecting the two classes of analogous reactions by the same theory. This consisted in conceiving, that in the formation of a hydrated acid, a compound radical is produced in combination with hydrogen ; so that hydrated sulphuric acid is the hydrogen-compound of SO_4, in the same way as hydrochloric acid is the hydrogen-compound of chlorine. There were many arguments in favour of this view, amongst which the most prominent was derived from the fact, that when a salt of the one class, as chloride of potassium, decomposes a salt of the other, as sulphate of silver, the result is exactly in conformity with what must occur on the supposition of the compound radical; and in like manner, the electrolytic decomposition of a sulphate moves the group SO_4 to the positive pole, where it either combines with a metal or undergoes decomposition.

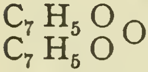
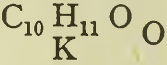
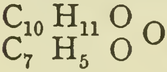
One of the strongest arguments against the view that the oxygen-acids contain water, is afforded by the results of recent researches (especially of MM. Laurent and Gerhardt) on the atomic weight of acids. Those chemists have rendered more definite and exact than they had been before, our ideas on the distinctions between monobasic, bibasic, and tribasic acids, and have clearly established that the correct expression of the atom of nitric acid must be such as contains half as much hydrogen at is contained in one atom of water (inasmuch as water is bibasic, and nitric acid monobasic). Of course this proportion may be as well established by doubling the atomic weight of water as by halving that of hydrated nitric acid; but either way it is clear that hydrated nitric acid cannot *contain* water.

Such was the position of the question, when an English chemist proved that the formation of ether from alcohol (which was considered chemically as the hydrate of ether), does not consist in a separation of two already formed compounds, but in a substitution of hydrogen by the organic radical ethyl. A similar fact M. Gerhardt has proved respecting a great number of organic acids, by preparing bodies which stand to them in the same relation as ether does to alcohol.

The researches of M. Cahours had led to the discovery of a series of bodies necessary for Gerhardt's process. These were obtained by the action of pentachloride of phosphorus on various hydrated organic acids, and consisted of chlorine combined with the oxygenized radical of the acid. Thus from benzoic acid was prepared the chloride of benzoil, $C_7 H_5 OCl$, and the corresponding bodies from cuminic, cinnamic, and various other acids. Gerhardt has since made by the same process the body $C_2 H_3 OCl$, which is the chloride of the radical of acetic acid, called *othyl.* Now, on bringing any one of these chlorides in contact with the potassium-salt of the corresponding acid, the chemical force of combination between chlorine and potassium induced the decomposition.

These results can be most simply stated in the form adopted by M. Gerhardt the discoverer, which consists in comparing the composition of these bodies with that of water, from which they are formed by the substitution of one or both atoms of hydrogen by organic radicals.

Thus water being represented by the formula $\begin{matrix}H\\H\end{matrix}O$, acetic acid is formed from it by the action of chloride of othyl $C_2 H_3OCl$, which forms $\begin{matrix}C_2H_3O\\H\end{matrix}O + HCl$, *i.e.* hydrated acetic acid and hydrochloric acid. If a second atom of chloride of othyl is made to act upon this acetic acid, or better upon the acetate of potash $\begin{matrix}C_2H_3O\\K\end{matrix}O$, we get, besides chloride of potassium, a compound $\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}O$ which when compared to the original type, may be considered as water having both its atoms of hydrogen replaced by the radical othyl, $C_2 H_3 O$. This compound is the anhydrous acetic acid which might be called the acetate of othyl, inasmuch as that radical has, in the formation of the compound, taken the place of the basic potassium in the acetate of potash.

In like manner, the anhydrous benzoic acid  $\begin{matrix} C_7H_5O \\ C_7H_5O \end{matrix} O$ was made by the action of the chloride of benzoil C_7H_5OCl on the benzoate of potash. It is a crystalline body, perfectly neutral to test paper, scarcely soluble in water, readily soluble in alcohol and ether. On continued boiling with water, it is converted into hydrated benzoic acid, one atom of the anhydride with one atom of water forming two atoms of the hydrated acid by an interchange of hydrogen and benzoil. Besides several of these anhydrous acids, Gerhardt has prepared some intermediate acids, analogous to the intermediate ethers, by combining two different radicals in the same group. Thus chloride of benzoil with cuminate of potash  $\begin{matrix} C_{10}H_{11}O \\ K \end{matrix} O$ formed cuminate of benzoil or benzocuminic acid  $\begin{matrix} C_{10}H_{11}O \\ C_7H_5O \end{matrix} O$; and in like manner, several other intermediate acids were prepared.

In conclusion, to this very brief exposition of this important series of discoveries, the Lecturer alluded to a feature of the development of the human mind in scientific research, which is strikingly illustrated by the substance and form of these results, and of which instances are probably to be found in the history of many others. The explanation of the above reactions consists in a combination of two modes of reasoning, which were developed by different schools, and for many years were used independently of one another. Gerhardt, to whose researches and writings some important steps in the doctrine of types are owing, formerly believed the truths which he saw from that point of view to be incompatible with the idea of radicals, but he now joins those chemists who find in each of these notions a necessary and most natural complement to the other.

May we not hope that such may be the result in other cases of difference of opinion on scientific questions, which the progress of knowledge will shew to have been owing to the incompleteness and one-sidedness of each view rather than to any thing absolutely erroneous in either?

NOTE ON THE DECOMPOSITION OF SULPHURIC ACID BY PENTACHLORIDE OF PHOSPHORUS.*

CHEMISTS have long been aware of the fact that some acids unite with bases in one proportion only, others in two or more proportions. Thus a given quantity of nitric acid forms with what is termed its equivalent of potash, a definite nitrate of potash; if less than this equivalent quantity of potash were added to the nitric acid, the product would be a mechanical mixture of the same nitrate of potash with uncombined nitric acid; if more than the equivalent of potash were added, the excess of alkali would remain uncombined. Sulphuric acid, on the other hand, is capable of forming two compounds with potash, and it depends upon the proportions in which the two substances are brought together whether the neutral or acid sulphate is formed.

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* [From *Proceedings of the Royal Society of London*, vol. vii. (1856), pp. 11-15.]

The number of compounds which an acid forms with one base is now considered as indicating its atomic weight. The weights of sulphuric and nitric acids which are respectively susceptible of neutralizing the same quantity of potash are termed *equivalent*, but these are by no means the same as their *atomic* weights. Sixty-three parts of nitric acid (nitrate of water) contains the same quantity of hydrogen as forty-five parts of sulphuric acid, and when they are neutralized by potash the whole of this hydrogen is removed and replaced by potassium ; and if neither of the acids could combine in any other proportion with potash, their atomic weights would be the same as their equivalent weights. But sulphuric acid also forms a potash compound in which half of its hydrogen is replaced by potassium, the other half remaining in the compound, whereas the smallest particles of nitric acid either exchange the whole or none of their hydrogen for potassium.

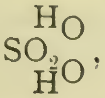
This fact is expressed in the simplest possible manner by the statement that the smallest indivisible particles of sulphuric acid contain two atoms of hydrogen, whilst those of nitric acid only contain one. Thus it is, that whereas the equivalent weights of the two acids are the quantities which contain the same amount of basic hydrogen, their atomic weights must be in the proportion of two equivalents of sulphuric to one of nitric acid. The simplest expression for an atom of nitric acid being empirically NO_3H, we shall accordingly represent an atom of sulphuric acid by the formula SO_4H_2. In like manner, an atom of common phosphoric acid, being tribasic, is expressed empirically by the formula PO_4H_3. The labours of Messrs. Laurent and Gerhardt greatly contributed to the establishment of these results, which are uncontroverted.

We have hitherto been accustomed to resort very freely to imaginary distinctions of form and arrangement of matter to explain the differences of properties; but of late years an opposite tendency has arisen, and chemists have felt the necessity of reducing their language and ideas to simpler and more consistent forms. This necessity was first felt in the most complex, *i. e.* the so-called organic part of chemistry. But the simplifications thus introduced have proved to be equally applicable to the inorganic part of the science; and their introduction is calculated to disengage, for the consideration of substantial differences of composition, the attention which has hitherto been absorbed by imaginary distinctions of form. Being unable to express the constitution of compounds without some formal artifice, we shall be able to see and compare their substantial differences most easily when all unnecessary variations of those formal artifices are eliminated. The success of this operation of course depends on our finding one form sufficiently general to replace the special and limited forms now employed.

In some papers published in the Journal of the Chemical Society two or three years ago, I endeavoured to show that the constitution of salts may be reduced to the type of water; that acids and bases being, truly, acid salts and basic salts, are perfectly conformable to the same principle; and that, amongst other things, the difference between monobasic and bibasic acids, &c. admits of a simple and easy explanation by it. The leading propositions in those papers have been adopted by several eminent chemists in this country and in France; and M. Gerhardt speedily enriched science with a series of brilliant and striking illustrations of their truth. As regards the constitution of bibasic acids, M. Gerhardt's results were, however, at variance with that theory; and he was led to represent them by formulæ equally inconsistent with his own previous views on the subject. I believe that this discrepancy is satisfactorily removed by the facts I have the honour of submitting to the consideration of the Society.

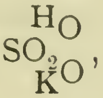
An atom of nitric acid, being eminently monobasic, is, as we have already shown, represented in the monobasic type $\begin{matrix}H\\H\end{matrix}O$ by the formula $\begin{matrix}(NO_2)\\H\end{matrix}O$, in which peroxide of nitrogen (NO_2) replaces one atom of hydrogen. In like manner, hydrate of potash $\left(\begin{matrix}H\\K\end{matrix}O\right)$ is obtained by replacing one atom of hydrogen in the type by its equivalent of potassium; and nitrate of potash $\left(\begin{matrix}NO_2\\K\end{matrix}O\right)$ by a simultaneous substitution of *one* atom of hydrogen by peroxide of nitrogen, the *other* by potassium. Sulphuric acid is formed from two atoms of water $\begin{matrix}\begin{matrix}H\\H\end{matrix}O\\\begin{matrix}H\\H\end{matrix}O\end{matrix}$; one of hydrogen from each is removed, and the two replaced by the indivisible radical SO_2. The series

Sulphuric acid.



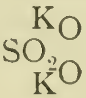
$$\begin{array}{l} \;\;HO \\ SO_2 \\ \;\;HO \end{array},$$

Acid sulphate of potash.



$$\begin{array}{l} \;\;HO \\ SO_2 \\ \;\;KO \end{array},$$

Neutral sulphate of potash.

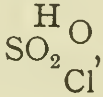


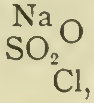
$$\begin{array}{l} \;\;KO \\ SO_2 \\ \;\;KO \end{array}$$

explains itself.

Chemists have long known how to remove the basylous constituents H, K, &c. of these salts, and to replace them by others. But it is only recently that they have learnt to remove the chlorous radicals SO_2, NO_2, &c. in a similar manner. To obtain the chloride of potassium from its sulphate, it is sufficient to bring the latter into liquid contact with chloride of barium ; but the same reagent would be powerless for the preparation of the chlorides of the radicals SO_2 or NO_2.

M. Cahours has shown us a reagent (the pentachloride of phosphorus) which is capable of forming from a great number of monobasic acids the chlorides of the acid radicals. Whilst extending our knowledge of the action of the body on monobasic and organic acids, and preparing numerous compounds of their radicals with one atom of chlorine, M. Gerhardt examined also the nature of its action upon bibasic acids and their compounds; and states that it consists of two successive phases, first, the liberation of the anhydrous acid, secondly, the substitution of two atoms of chlorine for one of oxygen in that anhydrous acid. These facts, if correct, would be unfavourable to the above view of the constitution of sulphuric and the other bibasic acids ; and M. Gerhardt adopted accordingly the old formulæ, representing in their composition an atom of water ready-formed, $SO_3\,H_2O$.

Confining my remarks for the present to the case of sulphuric acid, whose decomposition is doubtless typical of that of other bibasic acids, I may state as the result of numerous experiments with the most varied proportions of pentachloride and acid, performed on a scale of considerable magnitude, that the first action of the pentachloride consists in removing one atom of hydrogen and one of oxygen (empirically peroxide of hydrogen) from the acid, putting in an atom of chlorine in their place, and forming the compound  $SO_2\begin{matrix}H & \\ & O \\ & Cl\end{matrix}$, which is strictly intermediate between the hydrated acid and the final product SO_2Cl_2 formed by a repetition of the same process of substitution of chlorine for peroxide of hydrogen. The existence and formation of this body, which we may call chloro-hydrated sulphuric acid, furnishes the most direct evidence of the truth of the notion, that the bibasic character of sulphuric acid is owing to the fact of one atom of its radical SO_2 replacing or (to use the customary expression) being equivalent to two atoms of hydrogen. Had this radical been divisible like an equivalent quantity of a monobasic acid, we should have obtained a *mixture*, not a *compound* of the chloride with the hydrate,—or, at least, the products of decomposition of that mixture.

Chloro-hydrated sulphuric acid boils at 145° Cent., distilling without decomposition. The intensity of its action upon water varies according to the manner in which the two bodies are brought together. When poured rapidly into a large quantity of cold water, a portion of it sinks to the bottom, and only gradually dissolves as a mixture of hydrochloric and sulphuric acids. When a small quantity of water is added to the compound, the same decomposition takes place with explosive violence. The acid dissolves chloride of sodium on the application of a gentle heat with evolution of hydrochloric acid, giving rise to a compound of the formula  $\mathrm{SO}_2{}^{\overset{\mathrm{Na}}{\mathrm{O}}}_{\mathrm{Cl}}$, . When poured upon pieces of melted nitre at the atmospheric temperature, an effervescence takes place with evolution of a colourless vapour which possesses in a striking degree the odour of aqua regia. This vapour may be dissolved in various liquids, and when decomposed by water, yields nitric and hydrochloric acids. It is doubtless chloro-nitric acid, NO_2Cl. In like manner the chlorides of other inorganic acid radicals may be obtained, as from chlorates, perchlorates, sulphites, &c., but of these and other reactions I beg leave to defer any further account until the experiments now in hand are more advanced.

From the general resemblance of properties and identity of boiling-point of the chloro-hydrate with a compound discovered by Rose, and described by that eminent chemist as possessing empirically the composition $S_2O_5Cl_2$, I was led to suspect that the two might in reality be identical, which of course would require the addition of the elements of water to Rose's formula, and several experiments I have performed afford strong confirmation of that identity. The same compound is obtained by the action of dry hydrochloric acid on anhydrous sulphuric acid; and finally, I may mention that Mr. Railton obtained a small quantity of the same substance some weeks ago in my laboratory by the action of platinum-black at a high temperature on an imperfectly dried mixture of chlorine and sulphurous acid.

As regards the successive transformations effected in the pentachloride, I have observed the formation of Wurtz's oxychloride (the tribasic chloro-phosphoric acid ($POCl_3$)), and also of a compound boiling above 145°, probably PO_2Cl. Hydrated phosphoric acid is always found unless the amount of pentachloride added is very great.

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SKETCH OF A COURSE
OF
CHEMICAL PHILOSOPHY

BY

STANISLAO CANNIZZARO

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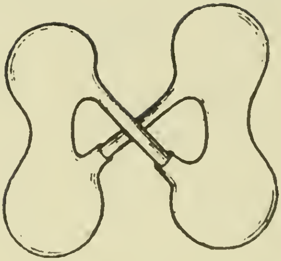

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PREFACE

THE value of the hypothesis of the Italian physicist Avogadro* as a systematising principle in chemistry was practically unrecognised for forty years after its publication. It had been, it is true, considered and in part applied by Dumas, Gerhardt, and others, but the young Italian chemist Cannizzaro was the first to show its consistent applicability to the selection of atomic weights, and to harmonise with it the results of other methods directed towards the same end.

The eminence of Cannizzaro as a teacher is plain in every page of the summary of his lecture course on chemical philosophy which is here translated. The facts are marshalled and their bearing explained with absolute mastery of pedagogic method, and one is impelled to the conclusion that Cannizzaro's students of 1858 must have had clearer conceptions of chemical theory than most of his scientific colleagues of a much later date.

Permission to publish this translation was received from the venerable chemist a few days before his death on 10th May 1910.

J. W.

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* Alembic Club Reprint, No. 4, p. 28.

LETTER OF
PROFESSOR STANISLAO CANNIZZARO
TO
PROFESSOR S. DE LUCA:

SKETCH OF A COURSE OF CHEMICAL PHILOSOPHY

*Given in the Royal University of Genoa.**

I BELIEVE that the progress of science made in these last years has confirmed the hypothesis of Avogadro, of Ampère, and of Dumas on the similar constitution of substances in the gaseous state; that is, that equal volumes of these substances, whether simple or compound, contain an equal number of molecules: not however an equal number of atoms, since the molecules of the different substances, or those of the same substance in its different states, may contain a different number of atoms, whether of the same or of diverse nature.

In order to lead my students to the conviction which I have reached myself, I wish to place them on the same path as that by which I have arrived at it—the path, that is, of the historical examination of chemical theories.

I commence, then, in the first lecture by showing how, from the examination of the physical properties of gaseous bodies, and from the law of Gay-Lussac on the volume relations between components and compounds, there arose almost spontaneously the hypothesis alluded to above, which was first of all enunciated by Avogadro, and shortly afterwards by Ampère. Analysing the conception of these two physicists, I show that it contains nothing contradictory to known facts, provided that we distinguish, as they did, molecules from atoms; provided that we do not confuse the criteria by which the number and the weight of the former are compared, with the criteria which serve to deduce the weight of the latter; provided that, finally, we have not fixed in our minds the prejudice that whilst the molecules of compound substances may consist of different numbers of atoms, the molecules of the various simple substances must all contain either one atom, or at least an equal number of atoms.

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* From *Il Nuovo Cimento*, vol. vii. (1858), pp. 321-366.

In the second lecture I set myself the task of investigating the reasons why this hypothesis of Avogadro and Ampère was not immediately accepted by the majority of chemists. I therefore expound rapidly the work and the ideas of those who examined the relationships of the reacting quantities of substances without concerning themselves with the volumes which these substances occupy in the gaseous state; and I pause to explain the ideas of Berzelius, by the influence of which the hypothesis above cited appeared to chemists out of harmony with the facts.

I examine the order of the ideas of Berzelius, and show how on the one hand he developed and completed the dualistic theory of Lavoisier by his own electro-chemical hypothesis, and how on the other hand, influenced by the atomic theory of Dalton (which had been confirmed by the experiments of Wollaston), he applied this theory and took it for his guide in his later researches, bringing it into agreement with the dualistic electro-chemical theory, whilst at the same time he extended the laws of Richter and tried to harmonise them with the results of Proust. I bring out clearly the reason why he was led to assume that the atoms, whilst separate in simple bodies, should unite to form the atoms of a compound of the first order, and these in turn, uniting in simple proportions, should form composite atoms of the second order, and why (since he could not admit that when two substances give a single compound, a molecule of the one and a molecule of the other, instead of uniting to form a single molecule, should change into two molecules of the same nature) he could not accept the hypothesis of Avogadro and of Ampère, which in many cases leads to the conclusion just indicated.

I then show how Berzelius, being unable to escape from his own dualistic ideas, and yet wishing to explain the simple relations discovered by Gay-Lussac between the volumes of gaseous compounds and their gaseous components, was led to formulate a hypothesis very different from that of Avogadro and of Ampère, namely, that equal volumes of simple substances in the gaseous state contain the same number of atoms, which in combination unite intact; how, later, the vapour densities of many simple substances having been determined, he had to restrict this hypothesis by saying that only simple substances which are permanent gases obey this law; how, not believing that composite atoms even of the same order could be equidistant in the gaseous state under the same conditions, he was led to suppose that in the molecules of hydrochloric, hydriodic, and hydrobromic acids, and in those of water and sulphuretted hydrogen, there was contained the same quantity of hydrogen, although the different behaviour of these compounds confirmed the deductions from the hypothesis of Avogadro and of Ampère.

I conclude this lecture by showing that we have only to distinguish atoms from molecules in order to reconcile all the experimental results known to Berzelius, and have no need to assume any difference in constitution between permanent and coercible, or between simple and compound gases, in contradiction to the physical properties of all elastic fluids.

In the third lecture I pass in review the various researches of physicists on gaseous bodies, and show that all the new researches from Gay-Lussac to Clausius confirm the hypothesis of Avogadro and of Ampère that the distances between the molecules, so long as they remain in the gaseous state, do not depend on their nature, nor on their mass, nor on the number of atoms they contain, but only on their temperature and on the pressure to which they are subjected.

In the fourth lecture I pass under review the chemical theories since Berzelius: I pause to examine how Dumas, inclining to the idea of Ampère, had habituated chemists who busied themselves with *organic substances* to apply this idea in determining the molecular weights of compounds; and what were the reasons which had stopped him half way in the application of this theory. I then expound, in continuation of this, two different methods—the one due to Berzelius, the other to Ampère and Dumas—which were used to determine formulæ in inorganic and in organic chemistry respectively until Laurent and Gerhardt sought to bring both parts of the science into harmony. I explain clearly how the discoveries made by Gerhardt, Williamson, Hofmann, Wurtz, Berthelot, Frankland, and others, on the constitution of organic compounds confirm the hypothesis of Avogadro and Ampère, and how that part of Gerhardt's theory which corresponds best with the facts and best explains their connection, is nothing but the extension of Ampère's theory, that is, its complete application, already begun by Dumas.

I draw attention, however, to the fact that Gerhardt did not always consistently follow the theory which had given him such fertile results; since he assumed that equal volumes of gaseous bodies contain the same number of molecules, only in the majority of cases, but not always.

I show how he was constrained by a prejudice, the reverse of that of Berzelius, frequently to distort the facts. Whilst Berzelius, on the one hand, did not admit that the molecules of simple substances could be divided in the act of combination, Gerhardt supposes that all the molecules of simple substances are divisible in chemical action. This prejudice forces him to suppose that the molecule of mercury and of all the metals consists of two atoms, like that of hydrogen, and therefore that the compounds of all the metals are of the same type as those of hydrogen. This error even yet persists in the minds of chemists, and has prevented them from discovering amongst the metals the existence of biatomic radicals perfectly analogous to those lately discovered by Wurtz in organic chemistry.

From the historical examination of chemical theories, as well as from physical researches, I draw the conclusion that to bring into harmony all the branches of chemistry we must have recourse to the complete application of the theory of Avogadro and Ampère in order to compare the weights and the numbers of the molecules; and I propose in the sequel to show that the conclusions drawn from it are invariably in accordance with all physical and chemical laws hitherto discovered.

I begin in the fifth lecture by applying the hypothesis of Avogadro and Ampere to determine the weights of molecules even before their composition is known.

On the basis of the hypothesis cited above, the weights of the molecules are proportional to the densities of the substances in the gaseous state. If we wish the densities of vapours to express the weights of the molecules, it is expedient to refer them all to the density of a simple gas taken as unity, rather than to the weight of a mixture of two gases such as air.

Hydrogen being the lightest gas, we may take it as the unit to which we refer the densities of other gaseous bodies, which in such a case express the weights of the molecules compared to the weight of the molecule of hydrogen = 1.

Since I prefer to take as common unit for the weights of the molecules and for their fractions, the weight of a half and not of a whole molecule of hydrogen, I therefore refer the densities of the various gaseous bodies to that of hydrogen = 2. If the densities are referred to air = 1, it is sufficient to multiply by 14.438 to change them to those referred to that of hydrogen = 1; and by 28·87 to refer them to the density of hydrogen = 2.

I write the two series of numbers, expressing these weights in the following manner:—

Names of Substances.	Densities or weights of one volume, the volume of Hydrogen being made = 1, *i.e.*, weights of the molecules referred to the weight of a whole molecule of Hydrogen taken as unity.	Densities referred to that of Hydrogen = 2, *i.e.*, weights of the molecules referred to the weight of half a molecule of Hydrogen taken as unity.
Hydrogen . . .	1	2
Oxygen, ordinary. .	16	32
Oxygen, electrised .	64	128
Sulphur below 1000° .	96	192
Sulphur* above 1000° .	32	64
Chlorine . . .	35·5	71
Bromine . . .	80	160
Arsenic . . .	150	300
Mercury . . .	100	200
Water	9	18
Hydrochloric Acid .	18·25	36·50†
Acetic Acid . . .	30	60

* This determination was made by Bineau, but I believe it requires confirmation.

† The numbers expressing the densities are approximate: we arrive at a closer approximation by comparing them with those derived from chemical data, and bringing the two into harmony.

Whoever wishes to refer the densities to hydrogen = 1 and the weights of the molecules to the weight of half a molecule of hydrogen, can say that the weights of the molecules are all represented by the weight of two volumes.

I myself, however, for simplicity of exposition, prefer to refer the densities to that of hydrogen = 2, and so the weights of the molecules are all represented by the weight of one volume.

From the few examples contained in the table, I show that the same substance in its different allotropic states can have different molecular weights, without concealing the fact that the experimental data on which this conclusion is founded still require confirmation.

I assume that the study of the various compounds has been begun by determining the weights of the molecules, *i.e.*, their densities in the gaseous state, without enquiring if they are simple or compound.

I then come to the examination of the composition of these molecules. If the substance is undecomposable, we are forced to admit that its molecule is entirely made up by the weight of one and the same kind of matter. If the body is composite, its elementary analysis is made, and thus we discover the constant relations between the weights of its components: then the weight of the molecule is divided into parts proportional to the numbers expressing the relative weights of the components, and thus we obtain the quantities of these components contained in the molecule of the compound, referred to the same unit as that to which we refer the weights of all the molecules. By this method I have constructed the following table :—

Name of Substance.	Weight of one volume, *i.e.*, weight of the molecule referred to the weight of half a molecule of Hydrogen = 1.	Component weights of one volume, *i.e.*, component weights of the molecule, all referred to the weight of half a molecule of Hydrogen = 1.	
Hydrogen	2	2 Hydrogen	
Oxygen, ordinary	32	32 Oxygen	
,, electrised	128	128 ,,	
Sulphur below 1000°	192	192 Sulphur	
,, above 1000° (?)	64	64 ,,	
Phosphorus	124	124 Phosphorus	
Chlorine	71	71 Chlorine	
Bromine	160	160 Bromine	
Iodine	254	254 Iodine	
Nitrogen	28	28 Nitrogen	
Arsenic	300	300 Arsenic	
Mercury	200	200 Mercury	
Hydrochloric Acid	36·5	35·5 Chlorine	1 Hydrogen
Hydrobromic Acid	81	80 Bromine	1 ,,
Hydriodic Acid	128	127 Iodine	1 ,,
Water	18	16 Oxygen	2 ,,
Ammonia	17	14 Nitrogen	3 ,,
Arseniuretted Hyd.	78	75 Arsenic	3 ,,
Phosphuretted Hyd.	35	32 Phosphorus	3 ,,
Calomel	235·5	35·5 Chlorine	200 Mercury
Corrosive Sublimate	271	71 ,,	200 ,,
Arsenic Trichloride	181·5	106·5 ,,	75 Arsenic
Protochloride of Phosphorus	138·5	106·5 ,,	32 Phosphorus
Perchloride of Iron	325	213 ,,	112 Iron
Protoxide of Nitrogen	44	16 Oxygen	28 Nitrogen
Binoxide of Nitrogen	30	16 ,,	14 ,,
Carbonic Oxide	28	16 ,,	12 Carbon
,, Acid	44	32 ,,	12 ,,
Ethylene	28	4 Hydrogen	24 ,,
Propylene	42	6 ,,	36 ,,
Acetic Acid, hydrated	60	4 ,, 32 Oxygen 24 Carbon	
,, anhydrous	102	6 Hydrogen 48 Oxygen 48 Carbon	
Alcohol	46	6 Hydrogen 16 Oxygen 24 Carbon	
Ether	74	10 Hydrogen 16 Oxygen 48 Carbon	

All the numbers contained in the preceding table are comparable amongst themselves, being referred to the same unit. And to fix this well in the minds of my pupils, I have recourse to a very simple artifice: I say to them, namely, "Suppose it to be shown that the half molecule of hydrogen weighs a millionth of a milligram, then all the numbers of the preceding table become concrete numbers, expressing in millionths of a milligram the concrete weights of the molecules and of their components: the same thing would follow if the common unit had any other concrete value," and so I lead them to gain a clear conception of the comparability of these numbers, whatever be the concrete value of the common unit.

Once this artifice has served its purpose, I hasten to destroy it by explaining how it is not possible in reality to know the concrete value of this unit; but the clear ideas remain in the minds of my pupils whatever may be their degree of mathematical knowledge. I proceed pretty much as engineers do when they destroy the wooden scaffolding which has served them to construct their bridges, as soon as these can support themselves. But I fear that you will say, "Is it worth the trouble and the waste of time and ink to tell me of this very common artifice?" I am, however, constrained to tell you that I have paused to do so because I have become attached to this pedagogic expedient, having had such great success with it amongst my pupils, and thus I recommend it to all those who, like myself, must teach chemistry to youths not well accustomed to the comparison of quantities.

Once my students have become familar with the importance of the numbers as they are exhibited in the preceding table, it is easy to lead them to discover the law which results from their comparison. "Compare," I say to them, "the various quantities of the same element contained in the molecule of the free substance and in those of all its different compounds, and you will not be able to escape the following law: *The different quantities of the same element contained in different molecules are all whole multiples of one and the same quantity, which, always being entire, has the right to be called an atom.*"

Thus:—

One molecule	of free hydrogen	contains	2	of hydrogen	= 2 × 1
,,	of hydrochloric acid	,,	1	,,	= 1 × 1
,,	of hydrobromic acid	,,	1	,,	= 1 × 1
,,	of hydriodic acid	,,	1	,,	= 1 × 1
,,	of hydrocyanic acid	,,	1	,,	= 1 × 1
,,	of water	,,	2	,,	= 2 × 1
,,	of sulphuretted hydrogen	,,	2	,,	= 2 × 1
,,	of formic acid	,,	2	,,	= 2 × 1
,,	of ammonia	,,	3	,,	= 3 × 1
,,	of gaseous phosphuretted hydrogen	,,	3	,,	= 3 × 1
,,	of acetic acid	,,	4	,,	= 4 × 1
,,	of ethylene	,,	4	,,	= 4 × 1
,,	of alcohol	,,	6	,,	= 6 × 1
,,	of ether	,,	10	,,	= 10 × 1

Thus all the various weights of hydrogen contained in the different molecules are integral multiples of the weight contained in the molecule of hydrochloric acid, which justifies our having taken it as common unit of the weights of the atoms and of the molecules. The atom of hydrogen is contained twice in the molecule of free hydrogen.

In the same way it is shown that the various quantities of chlorine existing in different molecules are all whole multiples of the quantity contained in the molecule of hydrochloric acid, that is, of 35.5; and that the quantities of oxygen existing in the different molecules are all whole multiples of the quantity contained in the molecule of water, that is, of 16, which quantity is half of that contained in the molecule of free oxygen, and an eighth part of that contained in the molecule of electrised oxygen (ozone). Thus :—

One molecule of free oxygen .	contains	32	of oxygen	= 2 × 16
,, of ozone . .	,,	128	,,	= 8 × 16
,, of water . .	,,	16	,,	= 1 × 16
,, of ether . . .	,,	16	,,	= 1 × 16
,, of acetic acid .	,,	32	,,	= 2 × 16
etc. etc.				

One molecule of free chlorine .	contains	71	of chlorine	= 2 × 35·5
,, of hydrochloric acid	,,	35·5	,,	= 1 × 35·5
,, of corrosive sublimate	,,	71	,,	= 2 × 35·5
,, of chloride of arsenic	,,	106·5	,,	= 3 × 35·5
,, of chloride of tin .	,,	142	,,	= 4 × 35·5
etc. etc.				

In a similar way may be found the smallest quantity of each element which enters as a whole into the molecules which contain it, and to which may be given with reason the name of atom. In order, then, to find the atomic weight of each element, it is necessary first of all to know the weights of all or of the greater part of the molecules in which it is contained and their composition.

If it should appear to any one that this method of finding the weights of the molecules is too hypothetical, then let him compare the composition of equal volumes of substances in the gaseous state under the same conditions. He will not be able to escape the following law: *The various quantities of the same element contained in equal volumes either of the free element or of its compounds are all whole multiples of one and the same quantity ;* that is, each element has a special numerical value by means of which and of integral coefficients the composition by weight of equal volumes of the different substances in which it is contained may be expressed. Now, since all chemical reactions take place between equal volumes, or integral multiples of them, it is possible to express all chemical reactions by means of the same numerical values and integral coefficients. The law enunciated in the form just indicated is a direct deduction from the facts: but who is not led to assume from this same law that the weights of equal volumes represent the molecular weights, although other proofs are wanting? I thus prefer to substitute in the expression of the law the word molecule instead of volume. This is advantageous for teaching, because, when the vapour densities cannot be determined, recourse is had to other means for deducing the weights of the molecules of compounds. The whole substance of my course consists in this: to prove the exactness of these latter methods by showing that they lead to the same results as the vapour density when both kinds of method can be adopted at the same time for determining molecular weights.

The law above enunciated, called by me the law of atoms, contains in itself that of multiple proportions and that of simple relations between the volumes; which I demonstrate amply in my lecture. After this I easily succeed in explaining how, expressing by symbols the different atomic weights of the various elements, it is possible to express by means of formulæ the composition of their molecules and of those of their compounds, and I pause a little to make my pupils familiar with the passage from gaseous volume to molecule, the first directly expressing the fact and the second interpreting it. Above all, I study to implant in their minds thoroughly the difference between molecule and atom. It is possible indeed to know the atomic weight of an element without knowing its molecular weight; this is seen in the case of carbon. A great number of the compounds of this substance being volatile, the weights of the molecules and their composition may be compared, and it is seen that the quantities of carbon which they contain are all integral multiples of 12, which quantity is thus the atom of carbon and expressed by the symbol C; but since we cannot determine the vapour density of free carbon we have no means of knowing the weight of its molecule, and thus we cannot know how many times the atom is contained in it. Analogy does not in any way help us, because we observe that the molecules of the most closely analogous substances (such as sulphur and oxygen), and even the molecules of the same substance in its allotropic states, are composed of different numbers of atoms. We have no means of predicting the vapour density of carbon; the only thing that we can say is that it will be either 12 or an integral multiple of 12 (in my system of numbers). The number which is given in different treatises on chemistry as the theoretical density of carbon is quite arbitrary, and a useless datum in chemical calculations; it is useless for calculating and verifying the weights of the molecules of the various compounds of carbon, because the weight of the molecule of free carbon may be ignored if we know the weights of the molecules of all its compounds; it is useless for determining the weight of the atom of carbon, because this is deduced by comparing the composition of a certain number of molecules containing carbon, and the knowledge of the weight of the molecule of this last would scarcely add a datum more to those which are already sufficient for the solution of the problem. Any one will easily convince himself of this by placing in the following manner the numbers expressing the molecular weights derived from the densities and the weights of the components contained in them:—

Names of Compounds of Carbon.	Weights of the molecules referred to the atom of Hydrogen.	Weights of the components of the molecules referred to the weight of the atom of Hydrogen taken as unity.	Formulæ, making $H = 1$ $C = 12$ $O = 16$ $S = 32$
Carbonic Oxide .	28	12 Carbon 16 Oxygen	CO
,, Acid .	44	12 ,, 32 ,,	CO^2
Sulphide of Carbon	76	12 ,, 64 Sulphur	CS^2
Marsh Gas . .	16	12 ,, 4 Hydrogen	CH^4
Ethylene . .	28	24 ,, 4 ,,	C^2H^4
Propylene . .	42	36 ,, 6 ,,	C^3H^6
Ether . . .	74	48 ,, 10 ,, 16 Oxygen	$C^4H^{10}O$
etc.	etc.	etc.	etc.

In the list of molecules containing carbon there might be placed also that of free carbon if the weight of it were known; but this would not have any greater utility than what we would derive by writing in the list one more compound of carbon; that is, it would do nothing but verify once more that the quantity of carbon contained in any molecule, whether of the element itself or of its compounds, is 12 or $n \times 12 = C^n$, n being an integral number.

I then discuss whether it is better to express the composition of the molecules of compounds, as a function of the molecules of the components, or if, on the other hand, it is better, as I commenced by doing, to express the composition of both in terms of those constant quantities which always enter by whole numbers into both, that is, by means of the atoms.

Thus, for example, is it better to indicate in the formula that one molecule of hydrochloric acid contains the weight of half a molecule of hydrogen and half a molecule of chlorine, or that it contains an atom of one and an atom of the other, pointing out at the same time that the molecules of both of these substances consist of two atoms?

Should we adopt the formulæ made with symbols indicating the molecules of the elements, then many coefficients of these symbols would be fractional, and the formula of a compound would indicate directly the ratio of the volumes occupied by the components and by the compounds in the gaseous state. This was proposed by Dumas in his classical memoir, *Sur quelques points de la Théorie atomique* (Annales de Chimie et de Physique, tom. 33, 1826).

To discuss the question proposed, I give to the molecules of the elements symbols of a different kind from those employed to represent the atoms, and in this way I compare the formulæ made with the two kinds of symbols.

Atoms or Molecules.	Symbols of the molecules of the Elements and formulæ made with these symbols.	Symbols of the atoms of the Elements and formulæ made with these symbols.	Nos. expressing their weights.
Atom of Hydrogen . . .	$\mathfrak{H}_{\frac{1}{2}}$	= H =	1
Molecule of Hydrogen . .	$\mathfrak{H}$	= H^2 =	2
Atom of Oxygen . . .	$\mathfrak{O}_{\frac{1}{2}} = \mathfrak{O}\mathfrak{z}_{\frac{1}{8}}$	= O =	16
Molecule of ordinary Oxygen .	$\mathfrak{O}$	= O^2 =	32
Molecule of electrised Oxygen (Ozone)	$\mathfrak{O}\mathfrak{z}$	= O^8 =	128
Atom of Sulphur . . .	$\mathfrak{S}_{\frac{1}{2}} = \mathfrak{S}\mathfrak{a}_{\frac{1}{6}}$	= S =	32
Molecule of Sulphur above 1000° (Bineau)	$\mathfrak{S}$	= S^2 =	64
Molecule of Sulphur below 1000°	$\mathfrak{S}\mathfrak{a}$	= S^6 =	192
„ Water . . .	$\mathfrak{H}\mathfrak{O}_{\frac{1}{2}} = \mathfrak{H}\mathfrak{O}\mathfrak{z}_{\frac{1}{8}}$	= H^2O =	18
„ Sulphuretted Hydrogen	$\mathfrak{H}\mathfrak{S}_{\frac{1}{2}} = \mathfrak{H}\mathfrak{S}\mathfrak{a}_{\frac{1}{6}}$	= H^2S =	34

These few examples are sufficient to demonstrate the inconveniences associated with the formulæ indicating the composition of compound molecules as a function of the entire component molecules, which may be summed up as follows:—

1°. It is not possible to determine the weight of the molecules of many elements the density of which in the gaseous state cannot be ascertained.

2°. If it is true that oxygen and sulphur have different densities in their different allotropic states, that is, if they have different molecular weights, then their compounds would have two or more formulæ according as the quantities of their components were referred to the molecules of one or the other allotropic state.

3°. The molecules of analogous substances (such as sulphur and oxygen) being composed of different numbers of atoms, the formulæ of analogous compounds would be dissimilar. If we indicate, instead, the composition of the molecules by means of the atoms, it is seen that analogous compounds contain in their molecules an equal number of atoms.

It is true that when we employ in the formulæ the symbols expressing the weights of the molecules, *i.e.*, of equal volumes, the relationship between the volumes of the components and those of the compounds follows directly; but this relationship is also indicated in the formulæ expressing the number of atoms; it is sufficient to bear in mind that the atom represented by a symbol is either the entire molecule of the free substance or a fraction of it, that is, it is sufficient to know the atomic formula of the free molecule. Thus, to take an example, it is sufficient to know that the atom of oxygen, O, is one-half of the molecule of ordinary oxygen and an eighth part of the molecule of electrised oxygen—to know that the weight of the atom of oxygen is represented by $\frac{1}{2}$ volume of free oxygen and $\frac{1}{3}$ of electrised oxygen. In short, it is easy to accustom students to consider the weights of the atoms as being represented either by a whole volume or by a fraction of a volume, according as the atom is equal to the whole molecule or to a fraction of it. In this system of formulæ, those which represent the weights and the composition of the molecules, whether of elements or of compounds, represent the weights and the composition of equal gaseous volumes under the same conditions. The atom of each element is represented by that quantity of it which constantly enters as a whole into equal volumes of the free substance or of its compounds; it may be either the entire quantity contained in one volume of the free substance or a simple sub-multiple of this quantity.

This foundation of the atomic theory having been laid, I begin in the following lecture—the sixth—to examine the constitution of the molecules of the chlorides, bromides, and iodides. Since the greater part of these are volatile, and since we know their densities in the gaseous state, there cannot remain any doubt as to the approximate weights of the molecules, and so of the quantities of chlorine, bromine, and iodine contained in them. These quantities being always integral multiples of the weights of chlorine, bromine, and iodine contained in hydrochloric, hydrobromic, and hydriodic acids, *i.e.*, of the weights of the half molecules, there can remain no doubt as to the atomic weights of these substances, and thus as to the number of atoms existing in the molecules of their compounds, whose weights and composition are known.

A difficulty sometimes appears in deciding whether the quantity of the other element combined with one atom of these halogens is 1, 2, 3, or *n* atoms in the molecule; to decide this, it is necessary to compare the composition of all the other molecules containing the same element and find out the weight of this element which constantly enters as a whole. When we cannot determine the vapour densities of the other compounds of the element whose atomic weight we wish to determine, it is necessary then to have recourse to other criteria to know the weights of their molecules and to deduce the weight of the atom of the element. What I am to expound in the sequel serves to teach my pupils the method of employing these other criteria to verify or to determine atomic weights and the composition of molecules. I begin by making them study the following table of some chlorides, bromides, and iodides whose vapour densities are known; I write their formulæ, certain of justifying later the value assigned to the atomic weights of some elements existing in the compounds indicated. I do not omit to draw their attention once more to the atomic weights of hydrogen, chlorine, bromine, and iodine being all equal to the weights of half a molecule, and represented by the weight of half a volume, which I indicate in the following table:—

	Symbol.	Weight.
Weight of the atom of Hydrogen or half a molecule represented by the weight of ½ volume .	H	1
Weight of the atom of Chlorine or half a molecule represented by the weight of ½ volume .	Cl	35·5
Weight of the atom of Bromine or half a molecule represented by the weight of ½ volume .	Br	80
Weight of the atom of Iodine or half a molecule represented by the weight of ½ volume .	I	127

These data being given, there follows the table of some compounds of the halogens:—

Names of the Chlorides.	Weights of equal volumes in the gaseous state, under the same conditions, referred to the weight of ½ volume of Hydrogen = 1; *i.e.*, weights of the molecules referred to the weight of the atom of Hydrogen = 1.	Composition of equal volumes in the gaseous state, under the same conditions, *i.e.*, composition of the molecules, the weights of the components being all referred to the weight of the atom of Hydrogen taken as unity, *i.e.*, the common unit adopted for the weights of atoms and of molecules.	Formulæ expressing the composition of the molecules or of equal volumes in the gaseous state under the same conditions.
Free Chlorine	71	71 of Chlorine	Cl^2
Hydrochloric Acid	36·5	35·5 ,, 1 of Hydrogen	HCl
Protochloride of Mercury or Calomel	235·5	35·5 ,, 200 of Mercury	$HgCl$
Bichloride of Mercury or Corrosive Sublimate	271	71 ,, 200 ,,	$HgCl^2$
Chloride of Ethyl	64·5	35·5 ,, 5 of Hydrogen 24 of Carbon	C^2H^5Cl
,, Acetyl	78·5	35·5 ,, 3 ,, 24 of Carbon 16 of Oxygen	C^2H^3OCl
,, Ethylene	99	71 of Chlorine 4 of Hydrogen 24 of Carbon	$C^2H^4Cl^2$
,, Arsenic	181·5	106·5 ,, 75 of Arsenic	$AsCl^3$
Protochloride of Phosphorus	138·5	106·5 ,, 32 of Phosphorus	PCl^3
Chloride of Boron	117·5	106·5 ,, 11 of Boron	BCl^3
Bichloride of Tin	259·6	142 ,, 117·6 of Tin	$SnCl^4$
,, Titanium	198	142 ,, 56 of Titanium	$TiCl^4$
Chloride of Silicon	170	142 ,, 28 of Silicon	$SiCl^4$
,, Zirconium	231	142 ,, 89 of Zirconium	$ZrCl^4$
,, Aluminium	267	213 ,, 54 of Aluminium	Al^2Cl^6
Perchloride of Iron	325	213 ,, 112 of Iron	Fe^2Cl^6
Sesquichloride of Chromium	319	213 ,, 106 of Chromium	Cr^2Cl^6

I stop to examine the composition of the molecules of the two chlorides and the two iodides of mercury. There can remain no doubt that the protochloride contains in its molecule the same quantity of chlorine as hydrochloric acid, that the bichloride contains twice as much, and that the quantity of mercury contained in the molecules of both is the same. The supposition made by some chemists that the quantities of chlorine contained in the two molecules are equal, and on the other hand that the quantities of mercury are different, is supported by no valid reason. The vapour densities of the two chlorides having been determined, and it having been observed that equal volumes of them contain the same quantity of mercury, and that the quantity of chlorine contained in one volume of the vapour of calomel is equal to that contained in the same volume of hydrochloric acid gas under the same conditions, whilst the quantity of chlorine contained in one volume of corrosive sublimate is twice that contained in an equal volume of calomel or of hydrochloric acid gas, the relative molecular composition of the two chlorides cannot be doubtful. The same may be said of the two iodides. Does the constant quantity of mercury existing in the molecules of these compounds, and represented by the number 200, correspond to one or more atoms? The observation that in these compounds the same quantity of mercury is combined with one or two atoms of chlorine or of iodine, would itself incline us to believe that this quantity is that which enters always as a whole into all the molecules containing mercury, namely, the atom; whence $Hg = 200$.

To verify this, it would be necessary to compare the various quantities of mercury contained in all the molecules of its compounds whose weights and composition are known with certainty. Few other compounds of mercury besides those indicated above lend themselves to this; still there are some in organic chemistry the formulæ of which express well the molecular composition; in these formulæ we always find $Hg^2 = 200$, chemists having made $Hg = 100$ and $H = 1$. This is a confirmation that the atom of mercury is 200 and not 100, no compound of mercury existing whose molecule contains less than this quantity of it. For verification I refer to the law of the specific heats of elements and of compounds.

I call the quantity of heat consumed by the atoms or the molecules the product of their weights into their specific heats. I compare the heat consumed by the atom of mercury with that consumed by the atoms of iodine and of bromine in the same physical state, and find them almost equal, which confirms the accuracy of the relation between the atomic weight of mercury and that of each of the two halogens, and thus also, indirectly, between the atomic weight of mercury and that of hydrogen, whose specific heats cannot be directly compared.

Thus we have—

Name of Substance.	Atomic weight.	Specific heat, *i.e.*, heat required to heat unit weight 1°.	Products of specific heats by atomic weights, *i.e.*, heat required to heat the atom 1.
Solid Bromine .	80	0·08432	6·74560
Iodine . .	127	0·05412	6·87324
Solid Mercury .	200	0·03241	6·48200

The same thing is shown by comparing the specific heats of the different compounds of mercury. Woestyn and Garnier have shown that the state of combination does not notably change the calorific capacity of the atoms ; and since this is almost equal in the various elements, the molecules would require, to heat them 1°, quantities of heat proportional to the number of atoms which they contain. If Hg = 200, that is, if the formulæ of the two chlorides and iodides of mercury are HgCl, HgI, $HgCl^2$, HgI^2, it will be necessary that the molecules of the first pair should consume twice as much heat as each separate atom, and those of the second pair three times as much ; and this is so in fact, as may be seen in the following table :—

Formulæ of the compounds of Mercury.	Weights of their molecules $=p$.	Specific heats of unit weight $=c$.	Specific heats of the molecules $=p\times c$.	Number of atoms in the molecules $=n$.	Specific heats of each atom $=\frac{p\times c}{n}$.
HgCl .	235·5	0·05205	12·257745	2	6·128872
HgI .	327	0·03949	12·91323	2	6·45661
$HgCl^2$.	271	0·06889	18·66919	3	6·22306
HgI^2 .	454	0·04197	19·05438	3	6·35146

Thus the weight 200 of mercury, whether as an element or in its compounds, requires to heat it 1° the same quantity of heat as 127 of iodine, 80 of bromine, and almost certainly as 35.5 of chlorine and 1 of hydrogen, if it were possible to compare these two last substances in the same physical state as that in which the specific heats of the above-named substances have been compared.

But the atoms of hydrogen, iodine, and bromine are half their respective molecules: thus it is natural to ask if the weight 200 of mercury also corresponds to half a molecule of free mercury. It is sufficient to look at the table of numbers expressing the molecular weights to perceive that if 2 is the molecular weight of hydrogen, the weight of the molecule of mercury is

200, *i.e.*, equal to the weight of the atom. In other words, one volume of vapour, whether of protochloride or protoiodide, whether of bichloride or of biniodide, contains an equal volume of mercury vapour ; so that each molecule of these compounds contains an entire molecule of mercury, which, entering as a whole into all the molecules, is the atom of this substance. This is confirmed by observing that the complete molecule of mercury requires for heating it 1°, the same quantity of heat as half a molecule of iodine, or half a molecule of bromine. It appears to me, then, that I can sustain that what enters into chemical actions is the half molecule of hydrogen and the whole molecule of mercury : both of these quantities are indivisible, at least *in the sphere of chemical actions actually known.* You will perceive that with this last expression I avoid the question if it is possible to divide this quantity further. I do not fail to apprise you that all those who faithfully applied the theory of Avogadro and of Ampère, have arrived at this same result. First Dumas and afterwards Gaudin showed that the molecule of mercury, differing from that of hydrogen, always entered as a whole into compounds. On this account Gaudin called the molecule of mercury monatomic, and that of hydrogen biatomic. However, I wish to avoid the use of these adjectives in this special sense, because to-day they are employed as you know in a very different sense, that is, to indicate the different capacity for saturation of the radicals.

The formulæ of the two chlorides of mercury having been demonstrated, I next compare them with that of hydrochloric acid. The atomic formulæ indicate that the constitution of the protochloride is similar to that of hydrochloric acid, if we consider the number of atoms existing in the molecules of the two ; if, however, we compare the quantities of the components with those which exist in their free molecules, then a difference is perceived. To make this evident I bring the atomic formulæ of the various molecules under examination into comparison with the formulæ made with the symbols expressing the weights of the entire molecules, placing them in the manner which you see below :—

	Symbols of the molecules of the elements and formulæ of their compounds made with these symbols, *i.e.*, symbols and formulæ representing the weights of equal volumes in the gaseous state.		Symbols of the atoms of the elements, and formulæ of their compounds made with these symbols.		Numbers expressing the corresponding weights.
Atom of Hydrogen . . .	$\mathfrak{H}\frac{1}{2}$	=	H	=	1
Molecule of Hydrogen . .	$\mathfrak{H}$	=	H^2	=	2
Atom of Chlorine . . .	$\mathfrak{Cl}\frac{1}{2}$	=	Cl	=	35·5
Molecule of Chlorine . .	$\mathfrak{Cl}$	=	Cl^2	=	71
Atom of Bromine . . .	$\mathfrak{Br}\frac{1}{2}$	=	Br	=	80
Molecule of Bromine . .	$\mathfrak{Br}$	=	Br^2	=	160
Atom of Iodine . . .	$\mathfrak{I}\frac{1}{2}$	=	I	=	127
Molecule of Iodine . . .	$\mathfrak{I}$	=	I^2	=	254
Atom of Mercury . . .	$\mathfrak{Hg}$	=	Hg	=	200
Molecule of Mercury . .	$\mathfrak{Hg}$	=	Hg	=	200
,, Hydrochloric Acid	$\mathfrak{H}\frac{1}{2}\mathfrak{Cl}\frac{1}{2}$	=	HCl	=	36·5
,, Hydrobromic Acid	$\mathfrak{H}\frac{1}{2}\mathfrak{Br}\frac{1}{2}$	=	HBr	=	81
,, Hydriodic Acid .	$\mathfrak{H}\frac{1}{2}\mathfrak{I}\frac{1}{2}$	=	HI	=	128
Mol. of protochloride of Mercury	$\mathfrak{Hg}\mathfrak{Cl}\frac{1}{2}$	=	$HgCl$	=	235·5
,, protobromide of Mercury	$\mathfrak{Hg}\mathfrak{Br}\frac{1}{2}$	=	$HgBr$	=	280
,, protoiodide of Mercury .	$\mathfrak{Hg}\mathfrak{I}\frac{1}{2}$	=	HgI	=	327
,, bichloride of Mercury .	$\mathfrak{Hg}\mathfrak{Cl}$	=	$HgCl^2$	=	271
,, bibromide of Mercury .	$\mathfrak{Hg}\mathfrak{Br}$	=	$HgBr^2$	=	360
,, biniodide of Mercury .	$\mathfrak{Hg}\mathfrak{I}$	=	HgI_2	=	454

The comparison of these formulæ confirms still more the preference which we must give to the atomic formulæ, which indicate also clearly the relations between the gaseous bodies. It is sufficient to recall that whilst the atoms of chlorine, bromine, iodine, and hydrogen are represented by the weight of ½ volume, the atom of mercury is represented by the weight of a whole volume.

I then come to the examination of the two chlorides of copper. The analogy with those of mercury forces us to admit that they have a similar atomic constitution, but we cannot verify this directly by determining and comparing the weights and the compositions of the molecules, as we do not know the vapour densities of these two compounds.

The specific heats of free copper and of its compounds confirm the atomic constitution of the two chlorides of copper deduced from the analogy with those of mercury. Indeed the composition of the two chlorides leads us to conclude that if they have the formulæ $CuCl$, $CuCl^2$, the atomic weight of copper indicated by Cu is equal to 63, which may be seen from the following proportions :—

	Ratio between the components expressed by numbers whose sum = 100.	Ratio between the components expressed by atomic weights.
Protochloride of Copper	36·04 : 63·96 Chlorine. Copper.	35·5 : 63 Cl. Cu.
Bichloride of Copper	52·98 : 47·02 Chlorine. Copper.	71 : 63 Cl^2. Cu.

Now 63 multiplied by the specific heat of copper gives a product practically equal to that given by the atomic weight of iodine or of mercury into their respective specific heats. Thus :

$$\underset{\text{Atomic weight of copper.}}{63} \times \underset{\text{Specific heat of copper.}}{0{\cdot}09515} = 6$$

The same quantity of heat is required to heat the weight of 63 of copper in its compounds through 1°. Thus :—

Formulæ of the compounds of Copper.	Weights of their molecules $=p$.	Specific heats of unit weights $=c$.	Specific heats of the molecules $=p \times c$.	Number of atoms in the molecules $=n$.	Specific heat of each atom $=\frac{p \times c}{n}$.
$CuCl$.	98·5	0·13827	13·619595	2	6·809797
CuI .	190	0·06869	14·0511	2	7·0255

After this comes the question, whether this quantity of copper which enters as a whole into the compounds, the calorific capacity of the atoms being maintained, is an entire molecule or a sub-multiple of it. The analogy of the compounds of copper with those of mercury would make us inclined to believe that the atom of copper is a complete molecule. But having no other proof to confirm this, I prefer to declare that there is no means of knowing the molecular weight of free copper until the vapour density of this substance can be determined.

I then go on to examine the constitution of the chlorides, bromides, and iodides of potassium, sodium, lithium, and silver. Each of these metals makes with each of the halogens only one well characterised and definite compound ; of none of these compounds is the vapour density known ; we are therefore in want of the direct means of discovering if in their molecules there are one, two, or more atoms of the halogens. But their analogies with the protochloride of mercury, $HgCl$, and with the protochloride of copper, $CuCl$, and the specific heats of the free metals and of their compounds make us assume that in the molecules of each of these compounds there is one atom of metal and one of halogen. According to this supposition, the atomic weight of potassium K = 39, that of sodium Na = 23, that of silver Ag = 108. These numbers multiplied by the respective specific heats give the same product as the atomic weights of the substances previously examined.

Name of Substance.	Atomic weight $=p$.	Specific heats of unit weight $=s$.	Specific heats of the atoms $=p \times c$.
Solid Bromine .	80	0·08432	6·74560
Iodine . .	127	0·05412	6·87324
Solid Mercury .	200	0·03241	6·48200
Copper . .	63	0·09515	6
Potassium . .	39	0·169556	6·612684
Sodium . .	23	0·2934	6·7482
Silver . .	108	0·05701	6·15708

Besides this, the specific heats of the chlorides, bromides, and iodides of these metals confirm the view that their molecules contain the same number of atoms of the two components. Thus :—

Formulæ and Names of the compounds.	Weights of their molecules $=p$.	Specific heats of unit weight $=c$.	Specific heats of the molecules $=p \times c$.	No. of atoms in the molecules $=n$	Specific heat of each atom $=\frac{p \times c}{n}$
KCl . Chl. of Potassium.	74·5	0·17295	12·884775	2	6·442387
NaCl . Chl. of Sodium.	58·5	0·21401	12·519585	2	6·259792
AgCl . Chl. of Silver.	143·5	0·09109	13·071415	2	6·535707
KBr . Brom. of Potassium	119	0·11321	13·47318	2	6·73659
NaBr . Brom. of Sodium.	103	0·13842	14·25726	2	7·12863
AgBr . Brom. of Silver.	188	0·07391	13·89508	2	6·94754
KI . . Iod. of Potassium.	166	0·08191	13·59706	2	6·79853
NaI . . Iodide of Sodium.	150	0.08684	13·0260	2	6·5130
AgI . . Iodide of Silver.	235	0·06159	14·47365	2	7·23682

Are the atoms of potassium, sodium, lithium, and silver equal to $\frac{1}{2}$ molecule, like that of hydrogen, or equal to a whole molecule, like that of mercury? As the vapour densities of these elements are wanting, we cannot answer the question directly; I will give you later some reasons which incline me to believe that the molecules of these elements, like that of hydrogen, are composed of two atoms.

Gold makes with each of the halogens two compounds. I show that the first chloride is analogous to calomel, *i.e.*, that it has AuCl as it formula. The atomic weight of gold deduced from the composition of the protochloride to which this formula is given corresponds to the law of specific heats, as may be seen from what follows:

$$\underset{\text{Au}}{196{\cdot}32} \quad \times \quad \underset{\substack{\text{Specific heat}\\ \text{of Gold.}}}{0{\cdot}03244} \quad = \quad 6{\cdot}3696208$$

I show in the sequel that the first or only chlorides of the following metals have a constitution similar to the bichloride of mercury and of that of copper, that is, for each atom of metal they contain two atoms of chlorine.

Not knowing the density in the gaseous state of these lower or only chlorides, we cannot show directly the quantity of chlorine existing in their molecules, yet the specific heats of these free metals and of their compounds show what I have said above. I write the quantities of these different elements combined with the weight of two atoms of chlorine in the lower or only chlorides, and confirm in these quantities the properties of the other atoms; I write the formulæ of the lower chlorides, bromides, and iodides all as MCl^2, and verify that they correspond to the laws of specific heats of compound substances.

Names of Substances.	Symbols and weights of the atoms.	Specific heats of unit weight.	Specific heats of the atoms.
Iodine . .	I = 127	0·05412	6·87324
Solid Mercury	Hg = 200	0·03241	6·48200
Copper . .	Cu = 63	0·09515	6
Zinc . .	Zn = 66	0·09555	6·30630
Lead . .	Pb = 207	0·0314	6·4998
Iron . .	Fe = 56	0·11379	6·37224
Manganese .	Mn = 55	0·1181	6·4955
Tin . .	Sn = 117·6	0·05623	6·612648
Platinum .	Pt = 197	0·03243	6·38871
Calcium . .	Ca = 40		
Magnesium .	Mg = 24		
Barium . .	Ba = 137		

Formulæ of the compounds.	Weights of their molecules $=p$.	Specific heats of unit weight $=c$.	Specific heats of the molecules $=p \times c$.	No. of atoms in the molecules $=n$.	Specific heat of each atom $=\frac{p \times c}{n}$.
$HgCl^2$.	271	0·06889	18·66919	3	6·22306
$ZnCl^2$.	134	0·13618	18·65666	3	6·21888
$SnCl^2$.	188·6	0·10161	19·163646	3	6·387882
$MnCl^2$.	126	0·14255	17·96130	3	5·98710
$PbCl^2$.	278	0·06641	18·46198	3	6·15399
$MgCl^2$.	95	0·1946	18·4870	3	6·1623
$CaCl^2$.	111	0·1642	18·2262	3	6·0754
$BaCl^2$.	208	0·08957	18·63056	3	6·21018
HgI^2 .	454	0·04197	19·05438	3	6·35146
PbI^2 .	461	0·04267	19·67087	3	6·55695

Some of the metals indicated above make other compounds with chlorine, bromine, and iodine, whose molecular weights may be determined and compositions compared ; in such cases the values found for the atomic weights are confirmed. Thus, for example, a molecule of perchloride of tin weighs 259.6, and contains 117.6 of tin ($=Sn$) and 142 of chlorine ($=Cl^4$). A molecule of perchloride of iron weighs 325, and contains 112 of iron ($=Fe^2$) and 213 of chlorine ($=Cl^6$).

For zinc there are some volatile compounds which confirm the atomic weight fixed by me. Chemists believing chloride of zinc to be of the same type as hydrochloric acid, made the atom of zinc $Zn = 33$, that is half of that adopted by me ; having then prepared some compounds of zinc with the alcohol radicals, they were astonished that, expressing the composition by formulæ corresponding to gaseous volumes equal to those of other well-known compounds, it was necessary to express the quantity of zinc contained in the molecule by Zn^2. This is a necessary consequence of the quantity of zinc represented by other chemists by Zn^2 being only a single atom, which is equivalent in its saturation capacity to two atoms of hydrogen. Since in the sequel of my lectures I return to this argument, you will therefore find it spoken of later in this abstract.

Are the atoms of all these metals equal to their molecules or to a simple sub-multiple of them ? I gave you above the reasons which make me think it probable that the molecules of these metals are similar to that of mercury ; but I warn you now that I do not believe my reasons to be of such value as to lead to that certainty which their vapour densities would give us if we only knew them.

Reviewing what I show in the lecture of which I have given you an abstract, we find it amounts to the following :—Not all the lower chlorides corresponding to the oxide with one atom of oxygen have the same constitution ; some of them contain a single atom of chlorine, others two, as may be seen in the following list :—

HCl	$HgCl$	$CuCl$	KCl	$NaCl$	$LiCl$	$AgCl$	$AuCl$
Hydrochloric acid.	Protochloride of mercury.	Protochloride of copper.	Chloride of potassium.	Chloride of sodium.	Chloride of lithium.	Chloride of silver.	Protochloride of gold.

$HgCl^2$	$CuCl^2$	$ZnCl^2$	$PbCl^2$	$CaCl^2$	$SnCl^2$	$PtCl^2$	etc. etc.
Bichloride of mercury.	Bichloride of copper.	Chloride of zinc.	Chloride of lead.	Chloride of calcium.	Protochloride of tin.	Protochloride of platinum.	

Regnault, having determined the specific heats of the metals and of many of their compounds, had observed that it was necessary to modify the atomic weights attributed to them, namely, to divide by 2 those of potassium, sodium, and silver, leaving the others unaltered ; or, *vice versa*, to multiply these latter by 2, leaving unaltered those of potassium, sodium, silver, and hydrogen. From this he drew the conclusion that the chlorides of potassium, sodium, and silver, are analogous to calomel (protochloride of mercury) and to protochloride of copper : on the other hand, that those of zinc, lead, calcium, etc., etc., are analogous to corrosive sublimate and to bichloride of copper ; but he supposed that the molecules of calomel and of the analogous chlorides all contained 2 atoms of metal and 2 of chlorine, whilst the molecules of corrosive sublimate and the other analogous chlorides contained 1 atom of metal and 2 of chlorine. Here follows the list of the formulæ proposed by Regnault.

H^2Cl^2	Hg^2Cl^2	Cu^2Cl^2	K^2Cl^2	Na^2Cl^2	Li^2Cl^2	Ag^2Cl^2	Au^2Cl^2
Hydrochloric acid.	Protochloride of mercury.	Protochloride of copper.	Chloride of potassium.	Chloride of sodium.	Chloride of lithium.	Chloride of silver.	Protochloride of gold.

$HgCl^2$	$CuCl^2$	$ZnCl^2$	$PbCl^2$	$CaCl^2$	etc. etc.
Bichloride of mercury.	Bichloride of copper.	Chloride of zinc.	Chloride of lead.	Chloride of calcium.	

In truth, using the data for specific heats alone, it is not possible to decide whether the molecules of the chlorides written in the first horizontal line are MCl or M^2Cl^2; the only thing that can be said is that they contain the same number of atoms of metal and of chlorine. But knowing the densities in the gaseous state of hydrochloric acid and of the two chlorides of mercury, and thus the weights of their molecules, we can compare their composition and decide the question; and I have already explained to you how I show to my pupils that the molecules of the two chlorides of mercury contain the same weight of mercury, and that the molecule of one of them contains the same quantity of chlorine as hydrochloric acid, *i.e.*, ½ molecule of free chlorine, whilst the molecule of the other chloride contains twice as much. This shows with certainty that the two formulæ Hg^2Cl^2, $HgCl^2$ are inexact, because they indicate that in the molecules of the two chlorides there is the same quantity of chlorine and different quantities of mercury, which is precisely the opposite of what is shown by the vapour densities. The formulæ proposed by me harmonise the results furnished by the specific heats and by the gaseous densities.

Now I wish to direct your attention to an inconsistency of Gerhardt. From the theory of Avogadro, Ampère, and Dumas, that is, from the comparison of the gaseous densities as representing the molecular weights, Gerhardt drew arguments in support of the view that the atoms of hydrogen, of chlorine, and of oxygen are half molecules; that the molecule of water contains twice as much hydrogen as that of hydrochloric acid; that in the molecule of ether there is twice as much of the radical ethyl as in that of alcohol; and that to form one molecule of anhydrous monobasic acid two molecules of hydrated acid must come together: and yet Gerhardt did not extend to the whole of chemistry the theory of Ampère, but arbitrarily, in opposition to its precepts, assumed that the molecules of chloride of potassium, of bichloride of mercury, in fact of all the chlorides corresponding to the protoxides, had the same atomic constitution as hydrochloric acid, and that the atoms of all the metals were, like that of hydrogen, a simple sub-multiple of the molecule.

I have already explained to you the reasons which show the contrary.

After having demonstrated the constitution of the chlorides corresponding to the oxides containing one atom of oxygen, I postpone the study of the other chlorides to another lecture, and now define what I mean by capacity for saturation of the various metallic radicals.

If we compare the constitution of the two kinds of chlorides, we observe that one atom of metal is now combined with one atom of chlorine, now with two; I express this by saying that in the first case the atom of metal is equivalent to 1 of hydrogen, in the second case to 2. Thus, for example, the atom of mercury, as it is in calomel, is equivalent to 1 of hydrogen, whereas in corrosive sublimate it is equivalent to 2; the atoms of potassium, sodium, and silver are equivalent to 1 of hydrogen: the atoms of zinc, lead, magnesium, calcium, etc., to 2. Now it is seen from the study of all chemical actions that the number of atoms of the various substances which combine with one and the same quantity of chlorine combine also with one and the same quantity of oxygen, of sulphur, or of any other substance, and *vice versa*. Thus, for example, if the same quantity of chlorine which combines with a single atom of zinc, or lead, or calcium combines with 2 atoms of hydrogen, of potassium, or of sodium, then the same quantity of oxygen or of any other substance which combines with a single atom of the first will combine with two of the second. This shows that the property possessed by the first atoms of being equivalent to 2 of the second depends on some cause inherent either in their own nature or in the state in which they are placed before combining. We express this constant equivalence by saying that each atom of the first has a saturation capacity twice that of each of the second. These expressions are not new to science, and we now only extend them from compounds of the second order to those of the first order.

For the same reasons given by chemists when they say that phosphoric acid assumes various saturation capacities without changing in composition, it may also be said that the atom of mercury and that of copper assume different saturation capacities according as they are found in the protochlorides or in the bichlorides. Thus, I express the fact that the atoms of these two metals being equivalent to 1 atom of hydrogen in the protochlorides, tend, in double decompositions, to take the place of a single atom of hydrogen, whilst in the bichlorides they tend to take the place of 2 atoms of hydrogen. For the same reason that we say there are three different modifications of phosphoric acid combined with various bases, we may also say that there are two different modifications of the same radical mercury or copper. I call the radicals of the protochlorides and of the corresponding salts, mercurous and cuprous; those of the bichlorides and of the corresponding salts are called mercuric and cupric radicals.

To express the various saturation capacities of the different radicals, I compare them to that of hydrogen or of the halogens, according as they are electro-positive or electro-negative. An atom of hydrogen is saturated by one of a halogen, and *vice versa.* I express this by saying that the first is a monatomic electro-positive radical, and the second a monatomic electro-negative radical: thus, potassium, sodium, lithium, silver, and the mercurous and cuprous radicals are monatomic electro-positive radicals. The biatomic radicals are those which, not being divisible, are equivalent to 2 of hydrogen or to 2 of chlorine; among the electro-positive radicals there are the metallic radicals of the mercuric and cupric salts, of the salts of zinc, lead, magnesium, calcium, etc., and amongst the electro-negative we have oxygen, sulphur, selenium, and tellurium, *i.e.*, the amphidic substances. There are, besides, radicals which are equivalent to three or more atoms of hydrogen or of chlorine, but I postpone the study of these until later.

Before finishing the lecture I take care to make clear that the law of equivalents must be considered as a law distinct from the law of atoms.

The latter in fact only says that the quantities of the same element contained in different molecules must be integral multiples of one and the same quantity, but it does not predict, for example, that an atom of zinc is equivalent to 2 of hydrogen not only in its compounds with chlorine, but in all other compounds in which they may replace each other. These constant relations between the numbers of atoms of various substances which displace one another, whatever may be the nature and the number of the other components, is a law which restricts the number of possible combinations, and sums up with greater definiteness all the cases of double decomposition.

I occupy the whole of the seventh lecture in studying some monatomic and biatomic radicals, namely, cyanogen and the alcohol radicals.

I have already told you the method which I faithfully follow for ascertaining the weights and numbers of the molecules of the various substances whose vapour densities can be determined. This method, applied to all the substances which contain alcohol radicals, permits us, so to speak, to follow the path from one molecule to another. To discover the saturation capacity of a radical, it is expedient to begin with the examination of a molecule in which it is combined with a monatomic radical: thus for electro-negative radicals I begin by examining the compounds with hydrogen or with any other monatomic electro-positive radical; and conversely, for the electro-positive radicals, I examine their compounds with chlorine, bromine, and iodine. Those electro-negative radicals which form a molecule with a single atom of hydrogen are monatomic; those which combine with 2 of hydrogen are biatomic, and so on. Conversely, the electro-positive radicals are monatomic if they combine with a single atom of halogen, biatomic if they combine with 2.

With these rules I establish—

1°. That cyanogen, CN, is a monatomic electro-negative radical, and that the molecule of free cyanogen contains twice the quantity of carbon and nitrogen contained in the molecule of the monocyanides; and that in this way cyanogen, CN, behaves in all respects like an atom of chlorine, Cl;

2°. That cacodyle, C^2H^6As, methyl, CH^3, ethyl, C^2H^5, and the other homologous and isologous radicals, are, like the atom of hydrogen, monatomic, and like it cannot form a molecule alone, but must associate themselves with another monatomic radical, simple or compound, whether of the same or of a different kind;

3°. That ethylene, C^2H^4, propylene, C^3H^6, are biatomic radicals analogous to the radicals of mercuric and cupric salts, and to those of the salts of zinc, lead, calcium, magnesium, etc.; and that these radicals, like the atom of mercury, can form a molecule by themselves.

The analogy between the mercuric salts and those of ethylene and propylene has not been noted, so far as I know, by any other chemist. All that I have expounded previously shows it with such clearness that it appears useless to stop and discuss it with you at length. In fact, just as 1 volume of the vapour of mercury, combining with an equal volume of chlorine, makes 1 volume of vapour of mercury bichloride, so 1 volume of ethylene combined with an equal volume of chlorine makes a single volume of vapour of chloride of ethylene—(oil of Dutch chemists). If the formula of this last is $C^2H^4Cl^2$, that of bichloride of mercury should be $HgCl^2$; and if this is the formula of the bichloride of mercury, the chlorides of zinc, lead, calcium, etc., must also be MCl^2; that is, the atoms of all these metals are, like ethylene and propylene, biatomic radicals. Observing that all the electro-positive monatomic radicals which can be weighed free in the gaseous state, behave like hydrogen, that is, cannot of themselves form molecules, it appears to me very probable that a capacity of saturation equal to that of hydrogen in atoms, or groups which can act as their substitutes, constantly coincides with the fact of their not being able to exist in the isolated state. This is the reason why, until there is proof to the contrary, I believe that the molecules of potassium, sodium, lithium, and silver in the free state are formed of two atoms, that is, are represented by the formulæ K^2, Na^2, Li^2, Ag^2.

Conversely, observing that if the atom of mercury (which tends to form a biatomic rather than a monatomic radical) like ethylene and propylene can exist in the free state, forming a distinct molecule by itself, it appears to me probable that the atoms of zinc, lead, and calcium should be endowed also with this property, that is, that the molecules of these metals should consist of a single atom. If this correspondence between the number of atoms contained in the molecule and the capacity of the saturation of the atom, or of the group which takes its place, is verified, we may sum up as follows: *the metallic radicals whose molecules enter as a whole into compounds are biatomic, those whose atom is half a molecule are monatomic.* You already perceive the importance of this correlation, which forces us to conclude that one molecule of mercury (in mercuric salts), or of zinc, or ethylene, or propylene, etc., is equivalent to a molecule of hydrogen, of potassium, or of silver; thus the former as well as the latter combines with an entire molecule of chlorine, yet with this important difference that the former, not being capable of division, forms a single molecule with two atoms of chlorine, whilst the latter, being divisible, makes with the two atoms of chlorine two distinct molecules. But before drawing a general conclusion of such importance, it is necessary to demonstrate somewhat better the accuracy of the data on which it is founded.

In the eighth lecture I begin to compare the mode of behaviour in some reactions of monatomic and biatomic radicals. The compound radicals indicated in the preceding lecture, since they form volatile compounds, frequently afford the means of explaining by analogy what holds good for metallic compounds, the molecular weights of which cannot often be determined directly, since few of them are volatile. This is the great benefit which the study of organic chemistry has rendered to chemistry in general.

In the use of formulæ I adhere to the following rules, which I state before representing by means of equations the various types of reaction :—

1°. I use the coefficients of the symbols in the position of the exponents only when I wish to express that the number of atoms indicated is contained in one and the same molecule ; in other cases I place the coefficient before the symbols. Thus, when I wish to indicate two atoms of free hydrogen as they are contained in a single molecule, I write H^2. If, however, I wish to indicate four atoms as they are contained in two molecules, I do not write H^4 but $2H^2$; for the same reason I indicate n atoms of free mercury by the formula $n\mathrm{Hg}$.

2°. Sometimes I repeat in the same formula more than once the same symbol to indicate some difference between one part and another of the same element. Thus I write acetic acid $C^2H^3HO^2$, to indicate that one of the four atoms of hydrogen contained in the molecule is in a state different from the other three, it alone being replaceable by metals. Occasionally I write the same symbol several times to indicate several atoms of the same element, only to place better in relief what occurs in some reactions.

3°. For this last reason I often write the various atoms of the same component or the residues of various equal molecules in vertical lines. Thus, for example, I indicate the molecule of bichloride of mercury, $HgCl^2$, as follows:—$\mathrm{Hg}\left\{\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right.$; the molecule of acetate of mercury, $C^4H^6HgO^4$, as follows: $\mathrm{Hg}\left\{\begin{matrix}C^2H^3O^2\\ C^2H^8O^2\end{matrix}\right.$; to indicate that the two atoms of chlorine or the two residues of acetic acid come from two distinct molecules of hydrochloric acid and of hydrated acetic acid.

4°. I indicate by the symbol $R^{\mathrm{i}}_{\mathrm{m}}$ any monatomic metallic radical whether simple or compound; and with the symbol $R^{\mathrm{ii}}_{\mathrm{m}}$ any biatomic metallic radical. If in the same formula or in the same equation I wish to indicate in general two or more monatomic radicals, the one different from the other, I add to the symbol the small letters *a*, *b*, *c*, etc., thus $R^{\mathrm{i}}_{\mathrm{ma}}\ R^{\mathrm{i}}_{\mathrm{mb}}$ indicates a single molecule formed of two different monatomic radicals; such are the so-called mixed radicals.

The molecules of the monatomic metallic radicals are represented by the formula $(R^{\mathrm{i}}_{\mathrm{m}})^2$; those of the biatomic radicals by the same symbol as for the radical existing in its compounds, since it is the character of these radicals to have the molecule formed of a single atom or of a single group which takes its place. You understand that in speaking of metallic radicals I include all those which can replace metals in saline compounds.

5°. Since all compounds containing in their molecule a single atom of hydrogen replaceable by metals behave similarly when they act on metals or on their compounds, it is convenient to adopt a general formula, and I shall use the following. In HX, X indicates all that there is in the molecule except metallic hydrogen; thus, for example, in the case of acetic acid, $X = C^2H^3O^2$, these being the components which together with H make up the molecule of hydrated acetic acid. Since there are compounds, also called acids, whose molecules contain two atoms of hydrogen replaceable by metals, and since owing to this last fact they behave in a similar manner towards molecules containing metals, I adopt for them the general formula H^2Y, indicating by Y all that there is in the molecules except the two atoms of hydrogen. I hasten to mention that when I indicate by X and by Y the things which in the molecules of acids are combined with H and H^2, I do not intend to affirm that X and H, or Y and H^2, are detached within the molecule as its two immediate components; but without touching the question of the disposition of the atoms within the molecule of acids, I only wish to indicate distinctly the part which is not changed in the transformation of the acid into its corresponding salts.

Before treating and discussing the various reactions, I remind my pupils once more that all the formulæ used by me correspond to equal gaseous volumes, the theory of Avogadro and Ampère being constantly the guiding thread which leads me in the study of chemical reactions.

This done, I now give very rapidly an abstract of what I explain in this lecture concerning some reactions of the monatomic and biatomic radicals. I always write the reaction of the molecule containing a monatomic radical alongside a corresponding one of a molecule containing a biatomic radical, in order that the comparison may be easier.

Direct Combination					
Of the Monatomic Metallic Radicals with the Halogens.			Of the Biatomic Metallic Radicals with the Halogens.		
* H^2 +	Cl^2 =	$2\ HCl$	Hg +	Cl^2 =	$HgCl^2$
1 molecule of hydrogen.	1 molecule of chlorine.	2 molecules of hydrochloric acid.	1 molecule of mercury.	1 molecule of chlorine.	1 molecule of bichloride of mercury.
K^2 +	Cl^2 =	$2\ KCl$	Zn +	Cl^2 =	$ZnCl^2$
1 molecule of potassium.	1 molecule of chlorine.	2 molecules of chloride of potassium.	1 molecule of zinc.	1 molecule of chlorine.	1 molecule of chloride of zinc.
†$(CH^3)^2$ +	Cl^2 =	$2\ CH^3Cl$	C^2H^4 +	Cl^2 =	$C^2H^4Cl^2$
1 molecule of methyl.	1 molecule of chlorine.	2 molecules of chloride of methyl.	1 molecule of ethylene.	1 molecule of chlorine.	1 molecule of chloride of ethylene.
$(R^{\text{i}}_{\text{m}})^2$ +	Cl^2 =	$2\ R^{\text{i}}_{\text{m}}Cl$	R^{ii}_{m} +	Cl^2 =	$R^{\text{ii}}_{\text{m}}Cl^2$
Apparent direct combination, in reality molecular double decomposition, in virtue of which two molecules of different kinds give two of the same kind.			True direct combination or union of two different entire molecules into a single molecule.		

* The direct combination of hydrogen and chlorine is expressed by some as $H + Cl = HCl$; in the equations used by me I always employ molecules.

† It appears that in practice this direct combination succeeds with difficulty, the chlorine having an action on the hydrogen of the radical; it has been indicated merely for comparison with that of ethylene.

From what precedes it may be observed that a complete molecule of chlorine, and thus of any halogen, always reacts with a complete molecule of a metallic radical; if the latter is monatomic it makes two molecules, if it is biatomic it forms only one.

SUBSTITUTIONS IN CHLORIDES, BROMIDES, AND IODIDES

Of one Monatomic Metallic Radical for another.

K^2	+	HCl HCl	=	H^2	+	KCl KCl
1 molecule of potassium.		2 molecules of hydrochloric acid.		1 molecule of hydrogen.		2 molecules of chloride of potassium.
H^2	+	$AgCl$ $AgCl$	=	Ag^2	+	HCl HCl
1 molecule of hydrogen.		2 molecules of chloride of silver.		1 molecule of silver.		2 molecules of hydrochloric acid.
Ag^2	+	HI HI	=	H^2	+	AgI AgI
1 molecule of silver.		2 molecules of hydriodic acid.		1 molecule of hydrogen.		2 molecules of iodide of silver.
$(R^{1}_{ma})^2$	+	$R^{1}_{mb}Cl$ $R^{1}_{mb}Cl$	=	$(R^{1}_{mb})^2$	+	$R^{1}_{ma}Cl$ $R^{1}_{ma}Cl$

Substitution without change in the number of molecules.

Of one Biatomic Metallic Radical for a Monatomic.

Zn	+	HCl HCl	=	H^2	+	$Zn\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$
1 molecule of zinc.		2 molecules of hydrochloric acid.		1 molecule of hydrogen.		1 molecule of chloride of zinc.
Zn	+	$AgCl$ $AgCl$	=	Ag^2	+	$Zn\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$
1 molecule of zinc.		2 molecules of chloride of silver.		1 molecule of silver.		1 molecule of chloride of zinc.
Hg	+	HI HI	=	H^2	+	$Hg\left\{\begin{matrix}I\\I\end{matrix}\right.$
1 molecule of mercury.		2 molecules of hydriodic acid.		1 molecule of hydrogen.		1 molecule of biniodide of mercury.
R^{ii}_{m}	+	$R^{1}_{m}Cl$ $R^{1}_{m}Cl$	=	$(R^{1}_{m})^2$	+	$R^{ii}_{m}\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$

Substitution with change in the number of molecules; 3 become 2.

From what is written in this table it is seen that two molecules of hydrochloric acid or of another analogous monochloride always react with a single molecule of metallic radical; if this is monatomic, they change into two molecules of monochloride, if it is biatomic into a single molecule of bichloride. The cause of the last difference consists in this: that the molecule of the monatomic radical is divisible into two; that of the biatomic radical, not being capable of division, collects into a single molecule the residues of two molecules of monochloride or monoiodide.

The biatomic radicals behave similarly to the acids containing 1 atom of monatomic metallic radicals (H, Ag, K); collecting into a single molecule the residues of two molecules of acids or of salts, as may be seen in the following comparative table.

Substitution in the Acids HX, and in general in the Salts $R^{i}_{m}X$,													
Of a Monatomic Metallic Radical, R^{i}_{ma}, for another, R^{i}_{mb}.							Of a Biatomic Metallic Radical, R^{ii}_{m}, for a Monatomic, R^{i}_{m}.						
K^2	+	$HAzO^3$ $HAzO^3$	=	H^2	+	$KAzO^3$ $KAzO^3$	Zn	+	$HAzO^3$ $HAzO^3$	=	H^2	+	$Zn\left\{\begin{matrix}AzO^3\\AzO^3\end{matrix}\right.$
1 molecule of potassium.		2 molecules of hydrated nitric acid.		1 molecule of hydrogen.		2 molecules of nitrate of potassium.	1 molecule of zinc.		2 molecules of hydrated nitric acid.		1 molecule of hydrogen.		1 molecule of nitrate of zinc.
Na^2	+	$HC^2H^3O^2$ $HC^2H^3O^2$	=	H^2	+	$NaC^2H^3O^2$ $NaC^2H^3O^2$	Zn	+	$HC^2H^3O^2$ $HC^2H^3O^2$	=	H^2	+	$Zn\left\{\begin{matrix}C^2H^3O^2\\C^2H^3O^2\end{matrix}\right.$
1 molecule of sodium.		2 molecules of hydrated acetic acid.		1 molecule of hydrogen.		2 molecules of acetate of sodium.	1 molecule of zinc.		2 molecules of hydrated acetic acid.		1 molecule of hydrogen.		1 molecule of acetate of zinc.
$(R^{i}_{ma})^2$	+	$R^{i}_{mb}X$ $R^{i}_{mb}X$	=	$(R^{i}_{mb})^2$	+	$R^{i}_{ma}X$ $R^{i}_{ma}X$	R^{ii}_{m}	+	$R^{i}_{m}X$ $R^{i}_{m}X$	=	$(R^{i}_{m})^2$	+	$R^{ii}_{m}\left\{\begin{matrix}X\\X\end{matrix}\right.$

These examples are sufficient to show that the compounds containing a monatomic metallic radical behave like the monochlorides: two molecules of these react with a single molecule of metallic radical, changing into two molecules if the latter is monatomic, into a single molecule if it is biatomic. We can prove more easily that the biatomic metallic radicals bind in a single molecule the residues X of two molecules $R^{\mathrm{i}}_{\mathrm{m}}X$, by comparing the double decompositions or mutual substitutions of the chlorides of the monatomic and biatomic radicals with the compound $R^{\mathrm{i}}_{\mathrm{m}}X$.

I write in the following table some examples of these double decompositions.

[TABLE

MUTUAL SUBSTITUTION OF THE COMPOUNDS CONTAINING A MONATOMIC RADICAL, $R^{i}_{m}X$,

With the Chlorides of the Monatomic Metallic Radicals $R^{i}_{m}Cl$.							With the Chlorides of the Biatomic Metallic Radicals $R^{ii}_{m}Cl^2 = R^{ii}_{m}\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$						
KCl	+	$HAzO^3$	=	HCl	+	$KAzO^3$	$Hg\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$	+	$HAzO^3$ $HAzO^3$	=	HCl HCl	+	$Hg\left\{\begin{matrix}AzO^3\\AzO^3\end{matrix}\right.$
1 molecule of chloride of potassium.		1 molecule of hydrated nitric acid.		1 molecule of hydrochloric acid.		1 molecule of nitrate of potassium.	1 molecule of bichloride of mercury.		2 molecules of hydrated nitric acid.		2 molecules of hydrochloric acid.		1 molecule of mercuric nitrate.
KCl	+	$AgC^2H^3O^2$	=	$AgCl$	+	$KC^2H^3O^2$	$Hg\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$	+	$AgC^2H^3O^2$ $AgC^2H^3O^2$	=	$AgCl$ $AgCl$	+	$Hg\left\{\begin{matrix}C^2H^3O^2\\C^2H^3O^2\end{matrix}\right.$
1 molecule of chloride of potassium.		1 molecule of acetate of silver.		1 molecule of chloride of silver.		1 molecule of acetate of potassium.	1 molecule of bichloride of mercury.		2 molecules of acetate of silver.		2 molecules of chloride of silver.		1 molecule of mercuric acetate.
C^2H^5, Cl	+	$AgC^2H^3O^2$	=	$AgCl$	+	$C^2H^5, C^2H^3O^2$	$C^2H^4\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$	+	$AgC^2H^3O^2$ $AgC^2H^3O^2$	=	$AgCl$ $AgCl$	+	$C^2H^5\left\{\begin{matrix}C^2H^3O^2\\C^2H^3O^2\end{matrix}\right.$
1 molecule of chloride of ethyl.		1 molecule of acetate of silver.		1 molecule of chloride of silver.		1 molecule of acetate of ethyl.	1 molecule of chloride of ethylene.		2 molecules of acetate of silver.		2 molecules of chloride of silver.		1 molecule of acetate of ethylene.
R^{i}_{ma}, Cl	+	$R^{i}_{mb}X$	=	$R^{i}_{mb}Cl$	+	$R^{i}_{ma}X$	$R^{ii}_{m}\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$	+	R^{i}_{m}, X R^{i}_{m}, X	=	$R^{i}_{m}Cl$ $R^{i}_{m}Cl$	+	$R^{ii}_{m}\left\{\begin{matrix}X\\X\end{matrix}\right.$

All the reactions indicated in this table may be summed up as follows :—Whatever is combined with one atom of hydrogen or any other equivalent radical =(X) replaces one atom of chlorine, and conversely is replaceable by the latter ; if an indivisible radical in the double decompositions is found combined in a single molecule with two atoms of chlorine, it will, if the chlorine is exchanged for X, remain combined in a single molecule with 2X.

That ethylene is combined with two atoms of chlorine in choride of ethylene, and that the acetate of ethylene contains in one molecule twice $C^2H^3O^2$, is shown by the comparison of the gaseous densities of these substances. From the vapour density and from the specific heats, it is further demonstrated that the molecule of corrosive sublimate, like that of chloride of ethylene, contains two atoms of chlorine. Hence the mercuric salts are constituted in a similar manner to those of ethylene, whilst the salts of potassium, sodium, and silver are formed like those of ethyl.

Having proved, then, as I think I have already sufficiently indicated, that the lower or only chlorides of iron, manganese, zinc, magnesium, calcium, barium, etc., are constituted like corrosive sublimate, that is, have the formula MCl^2, there can remain no further doubt that the salts which are obtained by means of these chlorides and of the monobasic acids, or of their salts, are all similar to those of ethylene, propylene, etc. These important conclusions may be summed up as follows :—

1°. Amongst the salts of monobasic acids only those of hydrogen, potassium, sodium, lithium, silver, together with mercurous and cuprous salts, are similar to those of methyl and ethyl, that is, to compounds of the alcohols containing a monatomic radical; all the other salts, of the so-called protoxides, are similar to those of ethylene and propylene, that is, to the compound ethers of the alcohols with biatomic radicals.

2°. A single molecule of the first is not sufficient to form the anhydrous acid and the metallic oxide; two molecules instead are required; but a single molecule of the second contains the components of the molecule of the anhydrous acid and of that of the protoxide. This becomes clear by bringing the following equations into comparison :—

$\begin{matrix}AgC^2H^3O^2\\AgC^2H^3O^2\end{matrix} =$	$\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}O +$	$C^4H^6O^3$	$Hg\left\{\begin{matrix}C^2H^3O^2\\C^2H^3O^2\end{matrix}\right. =$	$HgO +$	$C^4H^6O^3$
2 molecules of acetate of silver.	1 molecule of oxide of silver.	1 molecule of anhydrous acetic acid.	1 molecule of mercuric acetate.	1 molecule of oxide of mercury.	1 molecule of anhydrous acetic acid.
$\begin{matrix}C^2H^5, C^2H^3O^2\\C^2H^5, C^2H^3O^2\end{matrix} =$	$\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}O +$	$C^4H^6O^3$	$C^2H^4\left\{\begin{matrix}C^2H^3O^2\\C^2H^3O^2\end{matrix}\right. =$	$C^2H^4O +$	$C^4H^6O^3$
2 molecules of acetate of ethyl.	1 molecule of oxide of ethyl.	1 molecule of anhydrous acetic acid.	1 molecule of acetate of ethylene.	1 molecule of oxide of ethylene.	1 molecule of anhydrous acetic acid.
$\begin{matrix}R^{\text{i}}_{m}X\\R^{\text{i}}_{m}X\end{matrix} =$	$\left.\begin{matrix}R^{\text{i}}_{m}\\R^{\text{i}}_{m}\end{matrix}\right\}O +$	$(2X - O)$	$R^{\text{ii}}_{m}\left\{\begin{matrix}X\\X\end{matrix}\right. =$	$R^{\text{ii}}_{m}O +$	$(2X - O)$

The mercuric salts and the salts of zinc, etc., being similar to those of ethylene, it is probable that salts of this type exist containing the residues of two different monobasic acids. I indicate by what reactions they might be generated :—

$Hg\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$	+	$\begin{matrix}AgC^2H^3O^2\\AgC^2H^3O^2\end{matrix}$	=	$\begin{matrix}AgCl\\AgCl\end{matrix}$	+	$Hg\left\{\begin{matrix}C^2H^3O^2\\C^2H^3O^2\end{matrix}\right.$
1 molecule of bichloride of mercury.		2 molecules of acetate of silver.		2 molecules of chloride of silver.		1 molecule of acetate of mercury.
$Hg\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$	+	$\begin{matrix}AgC^2H^3O^2\\AgC^7H^5O^2\end{matrix}$	=	$\begin{matrix}AgCl\\AgCl\end{matrix}$	+	$Hg\left\{\begin{matrix}C^2H^3O^2\\C^7H^5O^2\end{matrix}\right.$
1 molecule of bichloride of mercury.		1 molecule of acetate and 1 of benzoate of silver.		2 molecules of chloride of silver.		1 molecule of benzacetate of mercury.
$C^2H^4\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$	+	$\begin{matrix}AgC^2H^3O^2\\AgC^7H^5O^2\end{matrix}$	=	$\begin{matrix}AgCl\\AgCl\end{matrix}$	+	$C^2H^4\left\{\begin{matrix}C^2H^3O^2\\C^7H^5O^2\end{matrix}\right.$
1 molecule of chloride of ethylene.		1 molecule of acetate and 1 of benzoate of silver.		2 molecules of chloride of silver.		1 molecule of benzacetate of ethylene.

Just as acetates are produced from anhydrous acetic acid and the oxides of biatomic metallic radicals, so from anhydrous benzacetic acid the benzacetates will be formed, as I indicate in the following equation :—

$$C^4H^6O^3 + R^{ii}_{m}O = R^{ii}_{m}C^4H^6O^4 = R^{ii}_{m}\left\{\begin{matrix}C^2H^3O^2\\C^2H^3O^2\end{matrix}\right.$$

$$C^9H^8O^3 + R^{ii}_{m}O = R^{ii}_{m}C^9H^8O^4 = R^{ii}_{m}\left\{\begin{matrix}C^2H^3O^2\\C^7H^5O^2\end{matrix}\right.$$

Having already proved that zinc is a biatomic radical, and that in consequence its atomic weight should be doubled, I stop to examine the reactions and the mode of formation of zinc ethyl, zinc methyl, etc. I show you by means of equations the method by which I interpret these reactions.

The vapour densities demonstrate the accuracy of the following formulæ corresponding to equal volumes: — C^2H^5Cl (chloride of ethyl) C^2H^5, H (hydride of ethyl) C^2H^5, C^2H^5 (free ethyl) C^2H^5, CH^3 (methyl ethyl), $Zn(C^2H^5)^2 = Zn\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right.$ (zinc ethyl).

$$\begin{array}{lclcl}
C^2H^5Cl & + \; H^2 & = & C^2H^5, H & + \; HCl \\
\begin{matrix} C^2H^5Cl \\ C^2H^5Cl \end{matrix} & + \; Zn & = & (C^2H^5)^2 & + \; Zn\left\{\begin{matrix} Cl \\ Cl \end{matrix}\right. \\
\begin{matrix} C^2H^5Cl \\ C^2H^5Cl \end{matrix} & + \; 2Zn & = & \left.\begin{matrix} C^2H^5 \\ C^2H^5 \end{matrix}\right\}Zn & + \; Zn\left\{\begin{matrix} Cl \\ Cl \end{matrix}\right. \\
\begin{matrix} C^2H^5Cl \\ C^2H^5Cl \end{matrix} & + \; \left.\begin{matrix} C^2H^5 \\ C^2H^5 \end{matrix}\right\}Zn & = & 2(C^2H^5)^2 & + \; Zn\left\{\begin{matrix} Cl \\ Cl \end{matrix}\right. \\
\begin{matrix} C^2H^5Cl \\ CH^3Cl \end{matrix} & + \; Zn & = & C^2H^5, CH^3 & + \; Zn\left\{\begin{matrix} Cl \\ Cl \end{matrix}\right. \\
\begin{matrix} C^2H^5Cl \\ CH^3Cl \end{matrix} & + \; 2Zn & = & \left.\begin{matrix} C^2H^5 \\ CH^3 \end{matrix}\right\}Zn & + \; Zn\left\{\begin{matrix} Cl \\ Cl \end{matrix}\right.
\end{array}$$

No one has yet demonstrated, as far as I know, the existence of the type of compound indicated in the last equation. But it being proved from the density of zinc ethyl vapour, and from its specific heat, that the complete molecule of zinc ethyl contains a single atom of zinc combined with two ethyl radicals, that is, with the molecule of the free radical, no one can deny that there will be prepared compounds containing a single atom of zinc combined with two different monatomic radicals. It may also be predicted that ethylene and propylene will form compounds in whose molecules an atom of zinc is combined with the biatomic radical.

I will give you later an account of some of my experiments directed to show the existence of the compounds just mentioned.

After having spoken of the mode of behaviour of the compounds containing monatomic or biatomic radicals with regard to monobasic acids, I examine the mode of behaviour with regard to those compounds which contain in each molecule two atoms of hydrogen, or, as they are called, the bibasic acids, to which I have given the general formula H^2Y.

To predict the reactions, it is sufficient to bear in mind what follows :—

1°. The two atoms of hydrogen are united in a single molecule by the forces of all the other components which together we call Y, hence what is equivalent to H^2 can enter into a single molecule with Y.

2°. What is combined with H^2 is equivalent to two atoms of chlorine Cl^2; hence in double decomposition H^2Y will act either on a single molecule of a bichloride ($=R^{II}_{m}Cl^2$) or on two molecules of a monochloride; what is combined with two atoms of chlorine, whether in one or in two molecules, will combine with Y; and H^2 combining with Cl^2 will always form two molecules of hydrochloric acid.

The examples of double decomposition which follow clearly show what I have just indicated.

DOUBLE DECOMPOSITIONS OF HYDRATED SULPHURIC ACID, H^2SO^4,

With the Monochlorides $R^{II}_{m}Cl$.	With the Bichlorides $R^{II}_{m}Cl^2$.
$\begin{matrix}Cl\\Cl\end{matrix} + H^2SO^4 = \begin{matrix}HCl\\HCl\end{matrix} + Na^2SO^4$	$Hg\left\{\begin{matrix}Cl\\Cl\end{matrix}\right. + H^2SO^4 = \begin{matrix}HCl\\HCl\end{matrix} + HgSO^4$
$\begin{matrix}Cl\\Cl\end{matrix} + Ag^2SO^4 = \begin{matrix}AgCl\\AgCl\end{matrix} + Na^2SO^4$	$Hg\left\{\begin{matrix}Cl\\Cl\end{matrix}\right. + Ag^2SO^4 = \begin{matrix}AgCl\\AgCl\end{matrix} + HgSO^4$
$\begin{matrix}H^5Cl\\H^5Cl\end{matrix} + Ag^2SO^4 = \begin{matrix}AgCl\\AgCl\end{matrix} + (C^2H^5)^2SO^4$	$C^2H^4\left\{\begin{matrix}Cl\\Cl\end{matrix}\right. + Ag^2SO^4 = \begin{matrix}AgCl\\AgCl\end{matrix} + C^2H^4SO^4$

In connection with this point I compare the formulæ of the oxy-salts proposed by me with those of Berzelius and of Gerhardt, and discuss the causes of the differences and of the coincidences, which may be summed up as follows :—

1°. All the formulæ given by Berzelius to the oxy-salts of the biatomic metallic radicals are the same as those proposed by me, whether the acid is monobasic or bibasic ; all these oxy-salts contain in each molecule the elements of a complete molecule of oxide and of a complete molecule of anhydrous acid.

2°. There correspond also to the formulæ proposed by me all those of Berzelius for sulphates and analogous salts, if we introduce the modification by Regnault, *i.e.*, if we consider the quantity of metal contained in the molecules of potassic, argentic, mercurous, and cuprous sulphates equal to 2 atoms, and those on the other hand of metal contained in the molecules of mercuric, cupric, plumbic, zincic, calcic, baric, etc., sulphates, equal to a single atom.

3°. The formulæ proposed by me for the oxy-salts of potassium, sodium, silver, hydrogen, methyl, and all the other analogous monatomic radicals with a monobasic acid, are equal to half the formulæ proposed by Berzelius and modified by Regnault, *i.e.*, each molecule of them contains the components of half a molecule of anhydrous acid and half a molecule of metallic oxide.

4°. The formulæ of Gerhardt coincide with those proposed by me only for the salts of potassium, sodium, silver, hydrogen, methyl, and all the other monatomic radicals, but not for those of zinc, lead, calcium, barium, and the other metallic protoxides ; Gerhardt having wished to consider all the metals analogous to hydrogen, which I have shown to be erroneous.

In the succeeding lectures I speak of the oxides with monatomic and biatomic radicals, afterwards I treat of the other classes of polyatomic radicals, examining comparatively the chlorides and the oxides; lastly, I discuss the constitution of acids and of salts, returning with new proofs to demonstrate what I have just indicated.

But of all this I will give you an abstract in another letter.

GENOA, 12*th March* 1858.

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The Foundations of the Theory of Dilute Solutions

PAPERS ON

OSMOTIC PRESSURE

BY J. H. VAN'T HOFF

AND ON

ELECTROLYTIC DISSOCIATION

BY SVANTE ARRHENIUS

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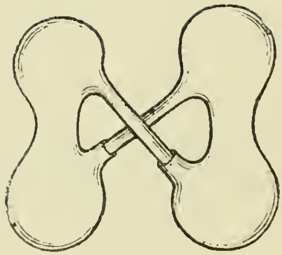

PREFACE

IN 1883 Arrhenius submitted to the Swedish Academy of Sciences a memoir entitled *Recherches sur la Conductibilité galvanique des Électrolytes*, and to the same body in 1885 van't Hoff presented his memoir *Lois de l'Équilibre chimique dans l'État dilué, gazeux ou dissous.* These communications contain the groundwork of the theories of electrolytic dissociation and of osmotic pressure, but it was only after the publication of the two papers here translated, which appeared in the first volume of the *Zeitschrift für physikalische Chemie* in 1887, that the theories became really fruitful. Each supplemented the other, and together they initiated a period of experimental and theoretical activity which is even yet not at an end. J. W.

October 1928.

FOUNDATIONS OF THE THEORY OF DILUTE SOLUTIONS

I

THE ROLE OF OSMOTIC PRESSURE IN THE ANALOGY BETWEEN SOLUTIONS AND GASES.[1]

By J. H. van't Hoff.

In the course of an investigation which aimed chiefly at the acquisition of knowledge regarding the laws that regulate chemical equilibrium in solution,[2] it gradually appeared that there is a fundamental analogy, nay almost an identity, with gases, more especially in their physical aspect, if only in solutions we consider the so-called osmotic pressure instead of the ordinary gaseous pressure. This analogy will be made evident as far as possible in the following memoir, physical properties being first considered.

I. Osmotic Pressure. Nature of the Analogy arising from its Introduction.

To gain in the first place a theoretical notion of the magnitude which will be chiefly dealt with in what follows, let us imagine a vessel A, completely filled with, say, an aqueous solution of sugar, and itself immersed in water B. If now the perfectly unyielding wall of the vessel is

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[[1] From *Zeitschrift für physikalische Chemie*, vol. i., pp. 481-508.]

[2] *Études de dynamique chimique*, p. 179; *Archives néerlandaises*, xx., 239; *K. Svenska Akademiens Handl.*, xxi., No. 17.

permeable to water and impermeable to the sugar dissolved in it, it is known that the attraction of the solution for water will cause water to enter into A, a process which will, however, soon come to an end through the pressure generated by the entry of a small amount of water. Under these circumstances there is equilibrium, and the pressure which will be exerted on the wall of the vessel we shall call in what follows osmotic pressure.

Of course this state of equilibrium may also be reached without entry of water into A, for instance, by connecting the vessel with a piston which exerts a pressure equal to the osmotic pressure. It is evident that by increasing or diminishing the pressure on the piston it is possible to effect whatever change of concentration in the solution we desire, water moving through the wall of the vessel in one direction or the other.

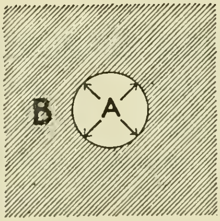

FIG. 1.

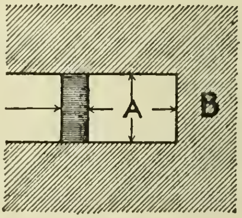

FIG. 2.

From the experimental standpoint this osmotic pressure may be described by means of one of Pfeffer's experiments.[1] In this experiment a cell of unglazed earthenware was used, which had been furnished with a membrane permeable only to water and not to sugar. The membrane is prepared by completely soaking the cell to expel air, filling it with a solution of potassium ferrocyanide and standing it in a solution of copper sulphate. The potassium and the copper salts meet after some time by diffusion about half way through the porous wall and form there a membrane of the desired character. A cell of this nature was then filled with a 1 per cent. sugar solution, closed by a stopper connected with a manometer, and immersed completely in water. By the entry of water the maximum osmotic pressure is gradually attained and is read off on the manometer at equilibrium. The 1 per cent. sugar solution, for example (which only suffered slight dilution by the entry of water) gave at 6.8° a pressure of 50.5 mm. of mercury, *i.e.*, about one-fifteenth of an atmosphere.

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[1] *Osmotische Untersuchungen*, Leipzig, 1877.

The peculiar membranes here described will in what follows be extensively employed under the name of "semipermeable membranes," even in cases where their preparation has perhaps not yet been experimentally effected. They permit a mode of treatment of solutions which presents the strongest resemblance to that usually adopted for gases, this being obviously due to the fact that the pressure characteristic of gases also comes into play for solutions in the form of osmotic pressure We wish to emphasise in this connection that we are not here dealing with a fanciful analogy, but with one which is fundamental; for the mechanism which according to our present conceptions produces gaseous pressure, and in solutions osmotic pressure, is essentially the same. In the first case it is due to the impacts of the gas-molecules on the containing walls, in the second to the impacts of the dissolved molecules on the semipermeable membrane. The molecules of the solvent present on both sides of the membrane, since they pass freely through it, need not be taken into consideration.

The great practical advantage which is offered by this analogy in the study of solutions, and which leads at once to quantitative results, is that the application of the second law of thermodynamics to solutions is made extremely easy, since reversible processes, with which this law is concerned, can now be carried out with the greatest simplicity. It has been already mentioned above that by the aid of a semipermeable cylinder, which is submerged in the solvent, we can by an appropriate pressure on the piston effect any desired change of concentration of the solution contained in the cylinder, just as a gas can be compressed or expanded, only that in the first case the solvent during these changes of volume moves through the cylinder wall. Such processes can in both cases be made reversible with equal ease by the pressure on the piston being equalised to the back pressure, that is, in the case of solutions, the osmotic pressure.

We shall make use of this practical advantage in what follows, especially for the study of the laws for "ideal solutions," that is, for solutions which are diluted to such an extent that they are comparable to "ideal gases," mutual action of the dissolved molecules, and also their volume in comparison to the volume of the solution, being negligible.[1]

[[1] Van't Hoff gave a more detailed account of his conception of ideal solutions in *K. Svenska Vet.-Akad. Handlingar*, vol. xxi., No. 17, p. 13 (1886):—

"For solutions a phenomenon easily observable betrays the mutual action of the dissolved particles; these actions give rise to the production of internal work in the act of dilution which appears as the equivalent amount of heat. In consequence the above laws are applicable only to solutions so dilute that the heat of dilution becomes negligible. It is clear that we thereby introduce no precise limit for the domain in which the laws are valid: in fact such a limit does not exist either for gases or for solutions. We can only speak of a limiting state which solutions approach as they become more and more dilute, without ever actually attaining it. It is only for a solution in this ideal state, which we shall call an 'ideal solution,' that the relations . . . to be developed in the sequel are rigorously exact."]

II. Boyle's Law for Dilute Solutions.

The analogy between dilute solutions and gases immediately takes on a more quantitative form when we consider that in both cases a change of concentration has a similar influence on the pressure, the two magnitudes being in the two cases proportional to each other.

This proportionality, which for gases goes under the name of Boyle's Law, can be proved for osmotic pressure experimentally from known data, and also theoretically.

Experimental Proof. Determination of Osmotic Pressure at Different Concentrations.—The following table contains Pfeffer's determinations[1] of the osmotic pressure P in sugar solutions of concentration C at room temperature (13.2° to 16.1°):

C. per cent.	P. mm.	P/C.
1	535	535
2	1016	508
2·74	1518	554
4	2082	521
6	3075	513

The approximately constant quotients P/C point to an actual proportionality between pressure and concentration.

Experimental Proof. Physiological Comparison of Osmotic Pressures.—The observations of de Vries[2] may be cited in support, since it appears from them that equal changes in concentration of solutions of sugar, potassium nitrate, and potassium sulphate have the same influence on osmotic pressure. This investigator compared by a physiological method the osmotic pressure of the solutions with that of the contents of a plant cell, the protoplasmic membrane of which shrinks when it is brought into contact with solutions having a greater attraction for water. On systematic comparison of different solutions of these three substances with the same cells, three so-called isotonic liquids, *i.e.*, solutions of the same osmotic pressure, were obtained. Cells of another plant were now employed, and four isotonic series of this kind were thus obtained, which then showed a similar proportion for their various concentrations. The following table gives the concentrations in gram-molecules per litre :—

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[1] *Osmotische Untersuchungen*, p. 71.

[2] "Eine Methode zur Analyse der Turgorkraft," *Pringsheims Jahrbücher*, xiv., 579 (1884).

Series.	KNO_3.	$C_{12}H_{22}O_{11}$.	K_2SO_4	$KNO_3=1$.	$C_{12}H_{22}O_{11}$.	K_2SO_4.
I	0·12	...	0·09	1	...	0·75
II	0·13	0·2	0·1	1	1·54	0·77
III	0·195	0·3	0·15	1	1·54	0·77
IV	0·26	0·4	...	1	1·54	...

Theoretical Proof.—Although these experiments render the proportionality between osmotic pressure and concentration highly probable, the theoretical proof is a welcome addition, especially as it is almost self-evident. If we consider osmotic pressure to be of kinetic origin, that is, as arising from the impacts of dissolved molecules, we have to prove proportionality between the number of impacts in unit time and the number of impinging molecules in unit volume. The method of proof is thus exactly the same as that adopted for Boyle's Law in ideal gases. On the other hand if we see in osmotic pressure the effect of an attraction for water, its magnitude is obviously proportional to the number of attracting molecules in unit volume, with the proviso (which is fulfilled in sufficiently dilute solutions) that the dissolved molecules are without action on one another, and that each contributes on its own account a constant amount to this attractive action.

III. Gay-Lussac's Law for Dilute Solutions.

Whilst the proportionality of concentration and osmotic pressure for constant temperature is self-evident, the proportionality between osmotic pressure and absolute temperature for constant concentration is not so manifest. However, this may be proved thermodynamically, and experimental data may be adduced in favour of the thermodynamical conclusions.

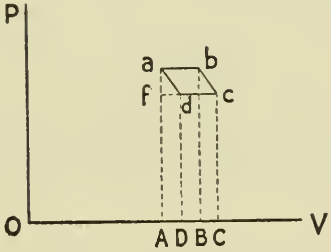

FIG. 3.

Theoretical Proof.—As has been already stated, reversible processes may be carried out by the aid of a piston and a cylinder with semi-permeable walls, and these we shall now employ for completing a thermodynamical cycle. If we use the same mode of representation as is adopted for gases, volume and pressure will be measured on OV and OP, the pressure being here osmotic pressure. Let the original volume (V cubic metres) be represented by OA, and let the original pressure (P kilograms) on the piston (1 square metre in area) be represented by Aa, and let the absolute temperature be T; then let the volume of the solution be increased by the small amount dV cubic metres (= AB) by movement of the piston through dV metres, while the temperature of the solution is kept constant by supply of the requisite quantity of heat. This quantity of heat can be at once determined, since T serves only to perform the known external work PdV by movement of the piston; internal work is not performed, the dilution being so great that the dissolved molecules are without mutual action. On this isothermal change ab follows the so-called isentropic change bc, in which heat neither leaves nor enters the system; the temperature then sinks by dT, after which the original state is regained by the second isothermal process cd and the isentropic process da. Now the second law of thermodynamics requires that of the heat PdV originally communicated to the system, the fraction $\frac{dT}{T}PdV$ is converted into work. This must be equal to the area of the quadrilateral figure abcd, whence we derive the following relation

$$\frac{dT}{T}PdV = \text{abcd} = \text{af}.\,\text{AB} = \text{af}.\,dV,$$

whence

$$P\frac{dT}{T} = \text{af}.$$

Here af is the change of osmotic pressure at constant volume caused by the change of temperature dT, or $\left(\frac{dP}{dT}\right)_v dT$, so that

$$\left(\frac{dP}{dT}\right)_v = \frac{P}{T}.$$

This equation on integration for constant volume gives

$$\frac{P}{T} = \text{const.},$$

that is, the osmotic pressure is proportional to the absolute temperature, if the volume (or concentration) remains the same, and thus there is exact correspondence to Gay-Lussac's Law for gases.

Experimental Proof. Determination of Osmotic Pressure at Different Temperatures.—The above theoretical result may first of all be compared with Pfeffer's results. Pfeffer found that without exception osmotic pressure increases with temperature, and it indeed appears that although the experimental results are not in themselves sufficient to establish the theorem conclusively, yet there is often an excellent correspondence between experiment and theory. If we calculate, for example, from the first of two experiments (made at two different temperatures with the same solution) the result of the second, assuming Gay-Lussac's Law, and then compare it with the direct result of experiment, we obtain the following numbers:

1. Cane-sugar—
   At 32° the observed pressure was 544 mm.
   At 14.15° the calculated pressure is 512, observed 510 mm.

2. Cane-sugar—
   At 36° the observed pressure was 567 mm.
   At 15.5° the calculated pressure is 529, observed 520.5 mm.

3. Sodium tartrate—
   At 36.6° the observed pressure was 1564 mm.
   At 13.3° the calculated pressure is 1443, observed 1431.6 mm.

4. Sodium tartrate—
   At 37.3° the observed pressure was 983 mm.
   At 13.3° the calculated pressure is 907, observed 908 mm.

Experimental Proof. Physiological Comparison of Osmotic Pressure.—Just as Boyle's Law for solutions received support from the circumstance that isotonic solutions of various substances retain their equality of osmotic pressure if the concentrations are varied in the same proportion, similarly it is a result supporting Gay-Lussac's Law that the isotony is maintained through equal alterations of temperature. This fact was established by Donders and Hamburger[1] working in the same way as de Vries, now, however, with animal cells (blood corpuscles). They found that solutions of potassium nitrate, sodium chloride, and cane-sugar which were isotonic with the corpuscles, and also with each other, at 0°, showed exactly the same behaviour at 34°, as the following table indicates:—

	0°	34°
KNO_3 . . .	1·052 to 1·03 per cent.	1·052 to 1·03 per cent.
NaCl . . .	0·62 ,, 0·609 ,,	0·62 ,, 0·609 ,,
$C_{12}H_{22}O_{11}$ . .	5·48 ,, 5·38 ,,	5·48 ,, 5·38 ,,

Experimental Proof of Boyle's and Gay-Lussac's Laws for Solutions. Soret's Experiments.[2]—The phenomena observed by Soret are most illuminating for the analogy between gases and solutions, where the influence of concentration and temperature on gas pressure and osmotic pressure is concerned. It appeared from them that just as for a quantity of gas in which there is a temperature difference, the warmer portion is the more dilute, so in solutions the warmer portion is also the more dilute, although here the time required to attain a state of equilibrium is much longer. The experiments were made in a vertical tube in such a way that the originally homogeneous solution was heated in the upper part at a constant temperature, and cooled in the lower part also to a definite temperature.

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[1] *Onderzoekingen gedaan in het physiologisch Laboratorium der Utrechtsche Hoogeschool* (3) ix., 26.

[2] *Archives des Sciences phys. et nat.* (3) ii., 48 ; *Ann. de Chim. et de Phys.* (5) xxii., 293.

Not only do Soret's observations provide a qualitative confirmation of the laws we are discussing; they also provide (at least in his final experiments) a welcome quantitative approximation to the values obtained from our theory. We should expect, as with gases, equilibrium to exist when isotony is reached, and so, since osmotic pressure is proportional both to concentration and to absolute temperature, that isotony of the two portions of the solution should occur when the product of these magnitudes is the same. If we calculate on this basis the concentration of the warm part of the solution from the observed concentration of the cold part and compare it with the value directly determined we find for solutions of copper sulphate:—

1. The cold portion at 20° contained 17.332 per cent. The warm portion at 80° should contain 14.3 per cent., as compared with 14.03 per cent. found.

2. The cold portion at 20° contained 29.867 per cent. The warm portion at 80° should contain 24.8 per cent., as compared with 23.871 per cent. found.

It must be admitted that Soret's older observations furnished less favourable results, but owing to the experimental difficulties too much importance need not be attributed to them.

IV. Avogadro's Law for Dilute Solutions.

We have considered in the main in what precedes only the changes undergone by osmotic pressure in solutions owing to alterations of concentration and temperature, and have shown the similarity which exists to the laws valid for gases. We now proceed to the direct comparison of the two analogous magnitudes, gaseous pressure and osmotic pressure, for one and the same substance. We have here obviously to deal with gaseous substances which can also be investigated in solution, and it will appear in fact that provided Henry's Law is obeyed, the osmotic pressure in solution is exactly equal to the gaseous pressure at the same temperature and concentration.

The proof is conducted by means of semipermeable membranes employed in a reversible cycle of operations at constant temperature with application of the second law of thermodynamics, which, as is known, in this case leads to the extremely simple result that there is no transformation of heat into work or *vice versa*, and consequently that the sum of the work throughout the cycle is zero.

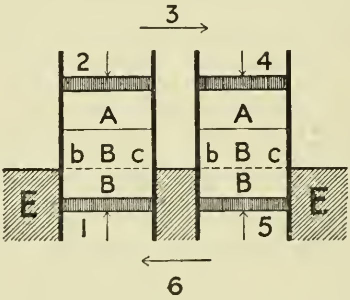

FIG. 4.

The cycle of operations is carried out by means of two similar double cylinders with pistons, one of which may be described. It contains in one portion a gas A, say oxygen, and in contact with this a solution B saturated with the gas under the conditions of experiment, say an aqueous solution; the wall bc is permeable to oxygen but not to water, the wall adjoining E, on the other hand, is permeable to water but not to oxygen, and is in contact externally with the solvent water E. By means of such a cylinder a reversible process may be carried out by simultaneously raising the pistons 1 and 2, so that gaseous oxygen is disengaged from its aqueous solution, and at the same time water is removed through the wall adjoining E, the change being conducted in such a manner that the concentrations of gas and solution remain unaltered. The only difference between the two cylinders is in the concentrations of oxygen within them, which can be defined as follows:—

Unit weight of the substance considered occupies in the left-hand vessel as gas and as solution the volumes v and V respectively, in the right-hand vessel the volumes $v+dv$ and $V+dV$. From Henry's Law we have then the following relation:—

$$v : V = (v+dv) : (V+dV)$$

so that

$$v : V = dv : dV.$$

Now let the pressure and the osmotic pressure for unit weight contained in unit volume of the gas or the solution be P and p respectively (which will later appear as equal), then by the application of Boyle's Law for the gas and the solution the pressures are $\frac{P}{v}$ and $\frac{p}{V}$ respectively.

We now raise the pistons 1 and 2 so as to liberate unit weight of the gas, and then augment the gaseous volume v by dv, in order that the gas may be brought to the concentration in the right-hand cylinder: we next by lowering the pistons 4 and 5 bring the gas previously liberated into solution, and diminish the volume $V+dV$ in which it is dissolved by dV by means of the cylinder with the semipermeable wall, and so complete the cycle. Here we have six amounts of work, the sum of which from what has been said above must be zero. If we indicate these by numbers, whose significance is obvious from the diagram, we have:

$$(1)+(2)+(3)+(4)+(5)+(6) = 0.$$

Now (2) and (4) are equal but of opposite sign, since they represent changes of volume v and $v+dv$ in opposed directions carried out at pressures which are inversely proportional to them. In the same way the sum of (1) and (5) must be zero, so that we obtain finally

$$(3)+(6) = 0.$$

Here (3) is the work done by the gas in expanding through dv against a pressure $\frac{P}{v}$, so

$$(3) = \frac{P}{v} \cdot dv,$$

whilst (6) is the work done on the solution by compressing it through dV against an osmotic pressure $\frac{p}{V}$. Consequently

$$(6) = -\frac{p}{V} \cdot dV,$$

so that

$$\frac{P}{v} \cdot dv = \frac{p}{V} \cdot dV,$$

and since $v : V = dv : dV$, we have $P = p$, which was to be proved.

The conclusion thus reached, which will be amply confirmed in what follows, is first of all a fresh support of the law of Gay-Lussac applied to solutions: if gas pressure and osmotic pressure are equal at the same temperature, a change of temperature will cause the same variation in them. But, in addition, the relation we have found admits of an important extension of Avogadro's law, which may now be applied to all solutions if we substitute osmotic for gaseous pressure: equal volumes of solutions at the same temperature and the same osmotic pressure contain the same number of molecules, namely, that which is contained at the same gas pressure and temperature in the same volume of a gas.

V. General Expression of the Laws of Boyle, Gay-Lussac, and Avogadro for Solutions and Gases.

The well-known formula which expresses the laws of Boyle and Gay-Lussac for gases, viz.,

$$PV = RT$$

is also applicable to solutions, for now we know that if the conception of osmotic pressure is introduced, these laws apply to liquids, and even with the same reservation, namely, that the dilution must be sufficiently great to allow us to neglect the reciprocal action of the dissolved particles and the volume occupied by them.

If we wish to incorporate Avogadro's law with the above expression, this may be done very simply by adopting Horstmann's proposal to consider in every case the kilogram-molecule of the substance concerned, *e.g.* 2 kg. hydrogen, 44 kg. carbon dioxide, etc. Then R in the above equation assumes the same value for all gases, for at the same temperature and pressure these quantities all occupy the same volume. If this value is calculated, the volume being expressed in cubic meters, and the pressure in kilograms per square meter, then choosing hydrogen at 0° and atmospheric pressure as standard of reference, we have

$$P = 10333, \quad V = 2/0.08956, \quad T = 273, \quad R = 845.05.$$

The general expression for the laws of Boyle, Gay-Lussac and Avogadro is thus

$$PV = 845\ T,$$

and is applicable in this form not only to gases, but to all solutions, provided P is taken to express osmotic pressure.

We give this expression a still simpler form for the purpose of subsequent application, by noting that the number of calories which is equivalent to a kilogram-meter, *i.e.*, the mechanical equivalent of heat $A = 1/423$, is very simply related to R, so that

$$AR = 2 \text{ (strictly about one-thousandth less)}$$

We can thus adopt the following form of the equation

$$APV = 2\ T,$$

which has the great practical advantage, that the amount of work done, which will be often used in the sequel, is very simply expressed by reducing it to calories.

We shall first ascertain the work, expressed in calories, if a gas or solution expands at constant pressure and temperature through the volume V, in which one kilogram-molecule is contained. This work is plainly $2\ T$. It may be noted that the constant pressure is maintained only if the total volume of gas or solution is very great in comparison with V, or if we are dealing with evaporation at the equilibrium pressure.

Secondly, we shall often have to speak of the thermal equivalent of the work which is performed on isothermal expansion, whether of a kilogram-molecule of a gas or of a solution in which this quantity of a dissolved substance is contained. If the pressure thereby sinks by a very small fraction ΔP, corresponding to an increase of volume ΔV, the work performed is $AP.\Delta V$, or $2\,\Delta T$.

VI. First Experimental Confirmation of Avogadro's Law in Solutions. Direct Determination of the Osmotic Pressure.

It might be expected a priori that Avogadro's Law, which we deduced as a consequence of Henry's Law, would not be confined to solutions of such substances as have by chance the gaseous form in ordinary circumstances. Nevertheless the confirmation of this supposition is very welcome in other cases, particularly in the following, which deals not with theoretical deductions, but with the direct results of experiment. In fact we find in Pfeffer's determinations of the osmotic pressure of sugar solutions[1] a striking confirmation of the proposition which is here defended.

The experiments relate to a 1 per cent. solution of sugar, *i.e.*, to a solution made from 1 gram of cane-sugar and 100 grams of water, which therefore contains 1 gram of sugar in 100.6 c.c. of solution. If we compare the osmotic pressure of this solution with the pressure of a gas, say hydrogen, which has the same number of molecules in 100.6 c.c., namely, in the instance chosen 2/342 grams ($C_{12}H_{22}O_{11} = 342$), there is an astonishing agreement. Since hydrogen at 1 atmosphere and 0° weighs 0.08956 g. per litre, and the above concentration leads to 0.0581 g. per litre, the pressure should be 0.649 atmospheres at 0°, and $0.649 (1 + 0.00367\,t)$ at t. If we compare with Pfeffer's data we obtain the following:

Temperature (t).	Osmotic Pressure.	$0{\cdot}649 (1 + 0{\cdot}00367\,t)$.
6·8	0·664	0·665
13·7	0·691	0·681
14·2	0·671	0·682
15·5	0·684	0·686
22	0·721	0·701
32	0·716	0·725
36	0·746	0·735

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[1] *Osmotische Untersuchungen*, Leipzig, 1877.

The directly determined osmotic pressure of a sugar solution is thus at the same temperature equal to the pressure of a gas, which contains as many molecules in a given volume as there are sugar molecules in the same volume of solution.

This relation can be extended from cane-sugar to other dissolved substances, such as invert sugar, malic acid, tartaric acid, citric acid, magnesium malate, magnesium sulphate, which according to the physiological investigations of de Vries[1] show the same osmotic pressure for equal molecular concentrations.

VII. Second Experimental Confirmation of Avogadro's Law in Solutions. Molecular Lowering of Vapour Pressure.

The relation existing between osmotic pressure and maximum vapour pressure, a relation which may be deduced from thermodynamical principles, is a suitable means of testing the laws above stated through the use of the experimental material lately collected by Raoult.

We place here in the forefront of our treatment a perfectly general principle altogether independent of what has been already developed, namely, that *isotony of solutions in the same solvent determines equality of vapour pressure.* This principle can easily be deduced by carrying out an isothermal cyclic process. For the purpose we take two solutions with the same vapour pressure and transfer reversibly a small quantity of the solvent in the state of vapour from one to the other by means of a cylinder and piston. This transference, on account of the equality of the vapour pressure, is effected without work being done; and therefore the solvent must be returned to the original solution without expenditure of work, for in the whole isothermal cycle no work is performed. Now, if we return the solvent by means of a semipermeable membrane separating the two solutions, the necessity of isotony may at once be perceived, since otherwise the change could not be effected without performance of work.

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[1] "Eine Methode zur Analyse der Turgorkraft," *loc. cit.*, p. 512.

If this principle is applied to dilute solutions by the aid of the laws developed for them, the simple conclusion may at once be deduced that equal molecular content of the dissolved substances is accompanied by equal vapour pressure of the solutions. This is nothing but the principle, recently discovered by Raoult,[1] of the constancy of molecular lowering of vapour pressure, for this magnitude is got by multiplying the molecular weight of the dissolved substance by the so-called relative lowering of the vapour pressure of a 1 per cent. solution, *i.e.*, by the proportional loss of vapour pressure of the solvent. Equality of the molecular lowering of vapour pressure is thus shown by solutions of the same molecular concentration, assuming proportionality of lowering of vapour pressure to concentration, an assumption which is true with close approximation. With ether, for example, the value of the molecular lowering for the thirteen dissolved substances investigated lies between 0.67 and 0.74 with a mean value of 0.71.

We can, however, carry this relationship a stage further and compare the different solvents with one another, and so reach the second law which Raoult likewise found experimentally. For this purpose we perform with a very dilute solution of P per cent. the following reversible cycle, which consists of two parts :—

1. The amount of solvent containing one kilogram-molecule (M) of the solute is removed by means of

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[1] *Comptes rendus*, civ., 976, 1430.

a piston and cylinder with semipermeable walls; the quantity of solution is so great that no change in concentration occurs, and the work done is therefore $2T$.

2. The $\frac{100M}{P}$ kilograms of solvent thus obtained are returned reversibly as vapour, first by evaporation at the vapour pressure of the solvent, then by expansion to the vapour pressure of the solution, and finally by condensation in contact with the solution. The kilogram-molecule of the solvent (M') would for this require an expenditure of work of $2T\Delta$, where Δ is the relative lowering of vapour pressure, and $\frac{100M}{P}$ kilograms would require $2T\Delta\frac{100M}{PM'}$. Now $\frac{\Delta}{P}.M$ is Raoult's molecular lowering of vapour pressure, which we shall call K, so that the above expression becomes $\frac{200TK}{M'}$.

The second law of thermodynamics requires that in this isothermal cycle the sum of the work should be zero, so that the work performed in the first portion should correspond to the work required in the second. We thus obtain

$$2T = \frac{200TK}{M'} \text{ or } 100K = M'.$$

This relation comprehends all the results of Raoult, and expresses once more what we have already deduced, that the molecular lowering of vapour pressure is independent of the nature of the dissolved substance. It shows also, as Raoult found, that the molecular lowering does not vary with the temperature. It contains finally the second principle of Raoult that the molecular lowering of vapour pressure is proportional to the molecular weight of the solvent, and is approximately one-hundredth part of this. The following numbers from Raoult's work show this relationship:—

Solvent.	Molecular Weight (M').	Molecular lowering (K).
Water	18	0·185
Phosphorus trichloride	137·5	1·49
Carbon bisulphide	76	0·80
Carbon tetrachloride	154	1·62
Chloroform	119·5	1·30
Amylene	70	0·74
Benzene	78	0·83
Methyl iodide	142	1·49
Ethyl bromide	109	1·18
Ether	74	0·71
Acetone	58	0·59
Methyl alcohol	32	0·33

VIII. Third Experimental Confirmation of Avogadro's Law in Solutions. Molecular Depression of Freezing-Point.

Here also there may be brought forward a general and perfectly strict theorem connecting the osmotic pressure with the freezing-point of a solution, namely:—*Solutions in the same solvent which have the same freezing-point are at this temperature isotonic.* This theorem, like the foregoing, can be proved by means of a cycle carried out at the freezing-point of the solutions, only that here the reversible transference of the solvent is made not as vapour but as ice. The solvent is again returned through a semipermeable membrane, and since the process cannot be accompanied by any performance of work, the solutions must be isotonic.

We can apply this principle to dilute solutions, and if we consider the relations developed in what has preceded, we arrive at once at the very simple deduction, that solutions which contain equal numbers of dissolved molecules in the same volume, and are thus isotonic according to Avogadro's Law, have the same freezing-point. This was actually discovered by Raoult and received its expression in the so-called "normal molecular freezing-point depression" which is shown by the great majority of dissolved substances, the product of the molecular weight and the freezing-point depression of a 1 per cent. solution being constant. The molecular depression thus refers to solutions of equal molecular concentrations, assuming proportionality of freezing-point depression and concentration, which holds good with close approximation. This value is for nearly all organic substances in aqueous solution equal to about 18.5.

We can, however, pursue the matter still further and deduce the above normal molecular depression of the freezing-point from other data with the help of Avogadro's principle for solutions. It is related in a necessary and simple way to the latent heat of fusion of the solvent, as may be shown by the following reversible cycle of operations involving the second law of thermodynamics. We consider a very dilute solution, of the percentage strength P, which shows a depression of the freezing-point Δ; the solvent itself freezes at T and its latent heat of fusion is W calories per kilogram.

1. The solution, exactly as in the preceding instance, is deprived at T, by means of a piston and cylinder with semipermeable walls, of a quantity of solvent which contains a kilogram-molecule (M) of the dissolved substance; the amount of solution is so great that there is no change of concentration caused by the process, and the work performed is thus $2T$.

2. The $\frac{100\,M}{P}$ kilograms of solvent thus obtained are allowed to freeze, $\frac{100\,MW}{P}$ calories being thereby evolved; the solution and solid solvent are then cooled through Δ degrees, and the latter is melted in contact with the solution, the calories previously obtained being now absorbed. Finally the temperature is raised through Δ degrees.

In this reversible cycle $\frac{100\,MW}{P}$ calories are raised through Δ degrees to T, which corresponds to a performance of work equal to $\frac{100\,MW\Delta}{PT}$. In this expression $\frac{M\Delta}{P}$ is the molecular lowering of the freezing-point, which we may represent by the letter t. The work done is thus $\frac{100\,Wt}{T}$, and this we found to be $2T$ in the first part of the cycle. Consequently

$$\frac{100\,Wt}{T} = 2T \quad \text{or} \quad t = 0.02\,\frac{T^2}{W}.$$

This relation is satisfactorily confirmed by experiment. For comparison we place the values calculated from the above formula alongside the molecular depressions of the freezing-point found by Raoult.[1]

Solvent.	T.	W.	$t = \frac{0{\cdot}02\,T^2}{W}$	Molecular Depressions.
Water . .	273	79	18·9	18·5
Acetic acid .	273 + 16·7	43·2[2, 3]	38·8	38·6
Formic acid .	273 + 8·5	55·6[2, 3]	28·4	27·7
Benzene . .	273 + 4·9	29·1[3]	53	50
Nitrobenzene .	273 + 5·3	22·3[3]	69·5	70·7

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[1] *Annales de Chim. et de Phys.* (5) xxviii.; (6) xi.

[2] Berthelot, *Essai de mécanique chimique.*

[3] Pettersson, *Journ. f. pr. Chem.* (2) xxiv., 129.

We may add that from the experimental value of the depression for ethylene dibromide, namely, 117.9, the latent heat of fusion was calculated to be 13; a subsequent determination kindly made by Mr Pettersson at my request yielded the expected value, namely, 12.94 as a mean.

IX. Application of Avogadro's Law to Solutions. Guldberg and Waage's Law.

Having till now stressed the physical side of the problem, in order to support as strongly as possible the principle we have developed, we next turn to its application to chemistry.

First of all, Avogadro's Law for solutions may clearly be used, as in the case of gases, to determine the molecular weight of substances in solution. This application is already an established fact, only here it does not consist in the measurement of pressure as in gases, where every molecular weight determination resolves itself into the measurement of pressure, volume, temperature, and weight; for solutions it involves determination of osmotic pressure, and practical methods for the measurement of this are wanting. Still this difficulty may be avoided by the measurement of the two magnitudes which have been shown above to be connected with osmotic pressure, namely, the depressions of vapour pressure and of freezing-point, instead of the osmotic pressure itself. Accordingly the proposal of Raoult already used for the determination of molecular weights, namely, to divide the relative lowerings of vapour pressure by 0.185 for 1 per cent. aqueous solutions, or their freezing-point depressions by 18.5, is a method which may be placed on a level with the method used for gases, the results obtained inspiring confidence in Avogadro's Law for solutions.

It is even more satisfactory that Guldberg and Waage's Law, so generally adopted for solutions, should be capable of appearing as a simple deduction from the above laws for dilute solutions. For the proof it is only necessary to conduct a reversible cyclic process at constant temperature, which can be done by means of semipermeable walls as easily for solutions as for gases.

Let us imagine two systems in equilibrium with each other, which may consist either of gaseous or dissolved substances, and which may be represented by the following symbolic equation:—

$$aM + a'M' + \ldots \rightleftharpoons a_1M_1 + a'_1M'_1 +, \ldots$$

where a is the number of molecules and M the molecular formula. This equilibrium exists in two different vessels, A and B (p. 30), at the same temperature but at different concentrations, which may be indicated by the partial pressures, or by the osmotic pressures, of the various substances. Let those in the vessel A be $PP' \ldots P_1P_1' \ldots$ etc., and those in B be greater by the amounts $dP\ dP' \ldots dP_1\ dP_1' \ldots$ etc.

The cycle to be performed consists in first introducing into A the quantity in kilograms of the first system expressed by the symbols of the foregoing equation, and then removing the corresponding amount of the second system, both having the concentrations pertaining to A. This is effected by introducing or withdrawing each of the substances by means of a special piston and cylinder which is separated from A by a membrane permeable to that substance only. If we are dealing with a solution, the cylinders themselves have semipermeable walls and are surrounded by the solvent.

After completion of the first process, each component of the second system is made to undergo a change of concentration which will make the concentration equal to that in B. Here, in accordance with what has been previously explained, an amount of work equal to $2\Delta T$ per kilogram-molecule is performed, Δ being the relative increase in pressure, namely, $\frac{dP}{P}$. For the quantity considered the work will be $2aT\frac{dP}{P}$.

Now by means of the vessel B the amount of the

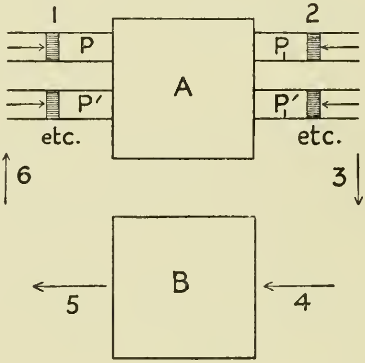

FIG. 5.

second system just obtained is reconverted into the first system, by the process described above, at the concentrations obtaining in B, and these are now brought to the original concentrations of A by appropriate changes of volume.

The cyclic process being conducted at constant temperature, the sum of the various amounts of work is zero, which may be indicated simply in the following way:—

$$(1) + (2) + (3) + (4) + (5) + (6) = 0.$$

Noting that (1) and (5) are transformations in opposite directions of the same quantity of the same materials at the same temperature, we have

$$(1) + (5) = 0;$$

for a similar reason

$$(2) + (4) = 0,$$

whence we obtain

$$(3) + (6) = 0.$$

The work (3) is, from what has been said, equal to $\Sigma 2a_1 T \frac{dP_1}{P_1}$, and (6) similarly is equal to $\Sigma 2aT \frac{dP}{P}$, whence we obtain

$$\Sigma\left(2a_1 T \frac{dP_1}{P_1} - 2aT\frac{dP}{P}\right) = 0$$

or

$$\Sigma\left(a_1 \frac{dP_1}{P_1} - a\frac{dP}{P}\right) = 0.$$

On integration this becomes

$$\Sigma(a_1 \log P_1 - a \log P) = \text{const.}$$

where P is proportional to the concentration or active mass C, which can then be substituted for P without affecting the constancy of the expression. We have then finally

$$\Sigma(a_1 \log C_1 - a \log C) = \text{const.}$$

which is nothing but the logarithmic form of Guldberg and Waage's formula.

X. Deviations from Avogadro's Law in Solutions. Modification of Guldberg and Waage's Law.

It has been attempted in the preceding pages to show the genetic connection between Guldberg and Waage's Law on the one hand and the laws for solutions on the other (namely, the laws of Boyle, Henry, Gay-Lussac, and Avogadro); it is the same connection as that which long since led in the case of gases to the derivation of the first-named law from thermodynamical principles.

We have now to develop the laws of chemical equilibrium further, and in the first place to investigate more closely the three principles from which Guldberg and Waage's Law was derivable.

If we confine our attention to "ideal solutions," then we have to consider a group of phenomena, which in view of the analogy between solutions and gases, must be placed in the same class as the so-called deviations from Avogadro's Law in the case of gases. For example, just as the pressure of ammonium chloride vapour is greater than that which Avogadro's Law predicts, so in several instances the osmotic pressure is also abnormally large; and as in the first case it was afterwards shown that there is here a decomposition into hydrochloric acid and ammonia, so we are led to suspect the same kind of thing in solutions. It must, however, be admitted that deviations of this kind in solutions are much more numerous, and are exhibited by substances, whose decomposition in the ordinary way could only with difficulty be assumed. In aqueous solution this class includes the majority of salts, the strong acids and bases, and so the existence of the so-called normal depression of freezing-point and of vapour pressure was only discovered when Raoult investigated organic compounds, which exhibit the normal behaviour almost without exception. Consequently it may seem daring to have placed Avogadro's Law so prominently in the foreground for such solutions, and I should not have adopted this course, had not Arrhenius privately written to me pointing out the probability that salts and the like are decomposed into ions. In fact the solutions so far investigated that obey Avogadro's Law are non-conductors, an observation which indicates that decomposition into ions does not occur, and a further experimental test may be made with the other solutions, since on the hypothesis of Arrhenius the deviations from Avogadro's Law may be calculated from the conductivities.

However that may be, it will be attempted in what follows to take these so-called deviations from Avogadro's Law also into consideration, and with the help in the first instance of Boyle's and Gay-Lussac's Laws for solutions to give the development of Guldberg and Waage's formula hereby made possible.

It is very easy to sketch the change in the expressions previously given when we take account of what has been mentioned above.

The general expression for the laws of Boyle, Gay-Lussac, and Avogadro, developed on p. 20,

$$APV = 2T$$

changes into

$$APV = 2iT$$

if the pressure is i times that postulated. In consequence the work done in reversible changes in solutions will be i times that previously given. This is the only change that need be made, and is easily applied to the above development of Guldberg and Waage's formula.

Recurring to the relation found (p. 31) for the final stage of the cycle

$$(3) + (6) = 0,$$

it is obvious that the amounts of work (3) and (6) which were formerly represented by $\Sigma 2a_1 T \frac{dP_1}{P_1}$ and $-\Sigma 2aT\frac{dP}{P}$ must now be multiplied by i, so that we obtain

$$\Sigma\left(a_1 i_1 \frac{dP_1}{P_1} - ai\frac{dP}{P}\right) = 0.$$

On integration this becomes

$$\Sigma(a_1 i_1 \log P_1 - ai \log P) = \text{const.}$$

or if we introduce the active mass C instead of the pressure which is proportional to it

$$\Sigma(a_1 i_1 \log C_1 - ai \log C) = \text{const.}$$

This is the logarithmic expression of Guldberg and Waage's formula in its new shape, which differs from the former merely by the introduction of the values of *i*.

It now remains to be shown that the new relation leads to a considerably better agreement with the facts than the original expression; an exact knowledge of the values of *i* is however necessary, and in attempting the proof desired we shall confine ourselves to aqueous solutions, for which alone sufficient experimental material is available.

XI. Determination of *i* for Aqueous Solutions.

As we have arrived at four different ways of establishing Avogadro's Law for solutions, we may make use of four corresponding ways to acquire a knowledge of the deviations from the law, that is, to determine the value of *i*. Since, however, the method based on the lowering of the freezing-point is, owing to the number and accuracy of the experiments, so greatly superior to the others, we shall confine ourselves entirely to it.

Reverting to the cycle which led to Avogadro's Law from freezing-point determinations, we have the relation (p. 27)

$$\frac{100\,Wt}{T} = 2T,$$

in which the second member represents the work associated with the reversible removal of that quantity of solvent which contains one kilogram-molecule dissolved in it. This must now be multiplied by i, so that

$$\frac{100\,Wt}{T} = 2\,iT.$$

Here we have a very simple means of determining i, for according to the above equation it must be proportional to t, the molecular depression of the freezing-point, since all the other quantities are constant, T being the melting-point on the absolute scale, and W the latent heat of fusion of the solvent. Now 18.5 is the molecular depression for cane-sugar, which (p. 21) obeys Avogadro's Law quite accurately, and for which therefore $i = 1$; for other substances i is therefore equal to the molecular depression divided by 18.5. Practically the same number is got by introducing into the above equation for T and W the values for ice, viz., 273 and 79, so that it will be used in the calculations which follow.

XII. Test of the Modified Law of Guldberg and Waage.

It is necessary for the purpose of applying the relation now proposed and of enabling the reader to carry out the comparison with the results of Guldberg and Waage's theory, to mention shortly the various forms which the latter has assumed in the course of its development. First of all, we shall give our own relation as a simple formula in which Guldberg and Waage's conceptions find expression, namely, as

$$\Sigma ai \log C = K \quad . \quad . \quad . \quad . \quad (1)$$

This formula only differs from that on p. 34 in that the terms for the components of the two systems are conceived as having opposite signs.

The original conception of the Norwegian scientists[1] is completely analogous, namely,

$$\Sigma k \log C = K \quad . \quad . \quad . \quad . \quad (2)$$

only that here the k referring to each component is to be determined by observation of the equilibrium considered.

When, however, Guldberg and Waage found from their experiments[2] that the coefficient k repeatedly assumed the value 1, they recast their law in the simplified form

$$\Sigma \log C = K \quad . \quad . \quad . \quad . \quad (3)$$

In their last memoir,[3] however, the modification is introduced that the number of molecules a must also be reckoned with, corresponding to the formula developed in the interval for gases on a thermodynamical basis, and so the following relation is obtained

$$\Sigma a \log C = K \quad . \quad . \quad . \quad . \quad (4)$$

In what has preceded we have termed this Guldberg and Waage's formula.

While this simplified formula with integral coefficients was being defended for solutions as well as gases by the Norwegian investigators, Lemoine,[4] from a consideration of Schloesing's experiments on the solubility of calcium carbonate in water containing carbonic acid, recently reverted to the original formula (2) with coefficients to be determined specially and having values not generally integral; otherwise, agreement between fact and theory could not be obtained.

In view of this uncertainty, the formula introduced by us has the advantage that the coefficients contained in it are definitely fixed from the beginning, and so its validity can be at once submitted to an experimental test. It will be seen when this is done that in the cases studied by Guldberg and Waage, owing to the special values of *i*, the simple formula, to which a general character was then given by these investigators, is entirely justified; that such simplification is in the majority of cases admissible is connected with the validity of Avogadro's Law for solutions which we have put forward in this paper. On the other hand, in the experiments of Schloesing discussed by Lemoine the simplification just mentioned is inadmissible, and the same fractional coefficients will be seen in the formula as Schloesing found experimentally.

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[1] *Christiania Videnskabs Selskabs Forhandlingar*, 1864.

[2] *Études sur les affinités chimiques*, 1867.

[3] *Journ. f. pr. chemie*, xix., 69.

[4] *Études sur les équilibres chimiques*, p. 266.

Before we can proceed to test our relationship further, it is necessary to adapt it also to the case in which partly undissolved substances may be present; this can be done very simply in the same manner for all the above formulæ, when we consider that such substances are always in a state of saturation in the solutions considered, *i.e.*, are at constant concentration. All concentrations referring to them may therefore be transferred from the first to the second member of the equation without affecting the constancy of the latter. Everything remains then as before, except that in the first member only dissolved substances are taken into account.

1. Let us turn first to Guldberg and Waage's observations. They studied in the first instance the equilibrium represented by the following equation:—

$$BaCO_3 + K_2SO_4 \rightleftharpoons BaSO_4 + K_2CO_3$$

and found according to their simplified formula

$$\log C_{K_2SO_4} - \log C_{K_2CO_3} = K.$$

Our formula leads practically to the same result, since for

K_2SO_4 $a = 1$ and $i = 2.11$, for K_2CO_3 $a = 1$ and $i = 2.26$, so that

$$\log C_{K_2SO_4} - 1.07 \log C_{K_2CO_3} = K.$$

This agreement between the two results persists for the sodium salts, where i for Na_2SO_4 and Na_2CO_3 is 1.91 and 2.18 respectively, so that

$$\log C_{Na_2SO_4} - 1.14 \log C_{NaCO_3} = K.$$

2. We cannot, however, expect these almost integral results for Schloesing's experiments,[1] which deal with the solubility of calcium carbonate in carbonic acid solution, that is the equilibrium expressed by the equation

$$CaCO_3 + H_2CO_3 \rightleftharpoons Ca(HCO_3)_2.$$

We therefore expect, since for carbonic acid $i = 1$, and for calcium hydrocarbonate $i = 2.56$

$$0.39 \log C_{H_2CO_3} - \log C_{Ca(HCO_3)_2} = K,$$

while Schloesing found

$$0.37866 \log C_{H_2CO_3} - \log C_{Ca(HCO_3)_2} = K.$$

For the corresponding case of barium salts the agreement is also very satisfactory. For barium hydrocarbonate $i = 2.66$, so that we obtain the result

$$0.376 \log C_{H_2CO_3} - \log C_{Ba(HCO_3)_2} = K,$$

experiment giving the following

$$0.38045 \log C_{H_2CO_3} - \log C_{Ba(HCO_3)_2} = K.$$

3. Let us now turn to Thomsen's experiments[2] on the action of sulphuric acid on sodium nitrate in solution. He arrived at the result that Guldberg and Waage correctly predicted the actual state of affairs. But this again is precisely one of those cases in which

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[1] *Comptes rendus*, lxxiv., 1552; lxxv., 70.

[2] *Thermochem. Untersuchungen*, i.

our relation and the formula of Guldberg and Waage lead to the same conclusion.

If the equilibrium is represented by the following equation:

$$Na_2SO_4 + HNO_3 \rightleftharpoons NaHSO_4 + NaNO_3$$

then Guldberg and Waage's relation requires

$$\log C_{Na_2SO_4} + \log C_{HNO_3} - \log C_{NaHSO_4} - \log C_{NaNO_3} = K.$$

Now we have

$$i_{Na_2SO_4} = 1.91, \quad i_{HNO_3} = 1.94, \quad i_{NaHSO_4} = 1.88, \quad i_{NaNO_3} = 1.82,$$

and thus obtain

$$1.05 \log C_{Na_2SO_4} + 1.06 \log C_{HNO_3} - 1.03 \log C_{NaHSO_4} - \log C_{NaNO_3} = K,$$

which amounts practically to the same thing.

If, on the other hand, we represent the equilibrium as

$$Na_2SO_4 + 2\,HNO_3 \rightleftharpoons H_2SO_4 + 2\,NaNO_3$$

Guldberg and Waage's formula gives

$$\log C_{Na_2SO_4} + 2 \log C_{HNO_3} - \log C_{H_2SO_4} - 2 \log C_{NaNO_3} = K.$$

whilst we obtain

$$\log C_{Na_2SO_4} + 2.03 \log C_{HNO_3} - 1.07 \log C_{H_2SO_4} - 1.91 \log C_{NaNO_3} = K.$$

again in almost complete agreement.

4. The investigations of Ostwald[1] on the action of hydrochloric acid on zinc sulphide, which relate to the equilibrium expressed by the following equation

$$ZnS + 2\,HCl \rightleftharpoons H_2S + ZnCl_2,$$

when we put

$$i_{HCl} = 1.98, \quad i_{H_2S} = 1.04, \quad i_{ZnCl_2} = 2.53$$

lead to the relation

$$3.96 \log C_{HCl} - 1.04 \log C_{H_2S} - 2.53 \log C_{ZnCl_2} = K.$$

[1] *Journ. für prakt. Chem.* (2) xix., 480.

Evidently when only hydrochloric acid and zinc sulphide were present at the beginning, the concentrations of hydrogen sulphide and zinc chloride were in this series equal. The original concentration of the hydrochloric acid was expressed by the volume V in which a definite amount of the acid was contained, the fraction which had been changed into zinc chloride by contact with zinc sulphide being indicated by x. Consequently we obtain

$$3.96 \log \frac{1-x}{V} - 3.57 \log \frac{x}{V} = \text{const.}$$

or

$$\frac{x}{(1-x)^{1.11}} V^{0.11} = \text{const.}$$

This function is in reality nearly constant

V.	x.	$\frac{x}{(1-x)^{1.11}} V^{0.11}$.
1	0·0411	0·043
2	0·038	0·0428
4	0·0345	0·0418
8	0·0317	0·0413

The experiments carried out in an analogous manner with sulphuric acid, where i for H_2SO_4 and $ZnSO_4$ is 2.06 and 0.98 respectively gave in the same way

$$\frac{x}{(1-x)^{1.02}} V^{0.02} = \text{const.},$$

which leads to a nearly constant value of x; this is in reality the experimental result as the following table shows:—

V.	x.
2	0·0238
4	0·0237
8	0·024
16	0·0241

5. The experiments of Engels[1] are also worthy of mention. They dealt with the solubility of magnesium carbonate in carbonic acid solution, which can be expressed as the equilibrium

$$MgCO_3 + H_2CO_3 \rightleftharpoons Mg(HCO_3)_2.$$

Here our formula, since *i* for magnesium carbonate is 2.64, leads to the relation

$$0.379 \log C_{H_2CO_3} - \log C_{Mg(HCO_3)_2} = K.$$

the values found being

$$0.37 \log C_{H_2CO_3} - \log C_{Mg(HCO_3)_2} = K.$$

6. The experiments of the same author[2] on the simultaneous solubility of ammonium sulphate and copper sulphate may also be quoted, the equilibrium being essentially

$$CuSO_4 + (NH_4)_2SO_4 \rightleftharpoons Cu(NH_4)_2(SO_4)_2.$$

As the double salt is always partially undissolved and *i* has for $CuSO_4$ and $(NH_4)_2SO_4$ the values 0.98 and 2 respectively, we here obtain the relation

$$0.49 \log C_{CuSO_4} + \log C_{(NH_4)_2SO_4} = K.$$

against the experimental expression

$$0.438 \log C_{CuSO_4} + \log C_{(NH_4)_2SO_4} = K.$$

7. Finally we may quote the experiments of Le Chatelier[3] on the equilibrium of basic mercuric sulphate and sulphuric acid, expressed by the equation

$$Hg_3SO_6 + 2H_2SO_4 \rightleftharpoons 3HgSO_4 + 2H_2O.$$

[1] *Comptes rendus*, c., 352, 444.

[2] *Ibid.*, cii., 113.

[3] *Ibid.*, xcviii., 675.

We expect in this case, since *i* for H_2SO_4 and $HgSO_4$ has the values 2.06 and 0.98 respectively, the relation

$$1.4 \log C_{H_2SO_4} - \log C_{HgSO_4} = K.$$

whereas we obtain as experimental result

$$1.58 \log C_{H_2SO_4} - \log C_{HgSO_4} = K.$$

In general then we may point to a very satisfactory agreement.

AMSTERDAM,
September 1887.

II.

ON THE DISSOCIATION OF SUBSTANCES IN AQUEOUS SOLUTION.[1]

By Svante Arrhenius.

In a memoir submitted to the Swedish Academy of Sciences on 14th October 1885 van't Hoff established both experimentally and theoretically the following very important generalisation of Avogadro's Law.[2]

"La pression exercée par les gaz à une température déterminée si un même nombre de molécules en occupe un volume donné, est égale à la pression osmotique qu'exerce dans les mêmes circonstances la grande majorité des corps, dissous dans les liquides quelconques."

This law was proved by van't Hoff so conclusively that little doubt can exist as to its entire accuracy. There remained, however, a certain difficulty to be overcome, namely, that the law was only valid for the "great majority of substances," a very considerable number of the aqueous solutions examined forming exceptions, since they exert a much higher osmotic pressure than is required by the law.

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[1] [From *Zeitschrift für physikalische Chemie*, vol. i., pp. 631-648. This memoir embodies two communications read before the Swedish Academy of Sciences and published in *Öfversigt af Kongl. Svenska Vetenskaps-Akademiens Forhandlingar*, 1887 :—

1. An attempt to calculate the dissociation (activity coefficients) of substances in aqueous solution. (Read 8th June 1887), p. 405.
2. On additive properties of dilute salt solutions. (Read 9th November 1887), p. 561.

The first of these papers is in Swedish ; the second in German.]

[2] Van't Hoff, Une propriété générale de la matière diluée, p. 43. *Sv. Vet.-Ak. Handlingar*, **21**, No. 17, 1886. (Also in *Archives néerlandaises* for 1885.)

When a gas shows a similar deviation from Avogadro's Law, the abnormality is explained by assuming that the gas is in a state of dissociation. A well-known example is afforded by the behaviour of chlorine, bromine, and iodine at high temperatures, these substances being regarded under the given conditions as split up into atoms.

The same expedient might be adopted to explain the exceptions to van't Hoff's Law, but so far it has not been used, probably owing to the novelty of the subject, the large number of known exceptions, and the grave objections on the chemical side which might be raised to such an explanation. The object of the present communication is to show that the hypothesis of dissociation of certain substances in aqueous solution is strongly supported by conclusions drawn from their electrical properties, and also that on closer consideration the chemical objections are appreciably lessened.

For the explanation of electrolytic phenomena we must postulate with Clausius[1] that a portion of the molecules of an electrolyte is dissociated into ions which move independently of one another. Since now the "osmotic pressure" which a substance dissolved in a liquid exerts on the walls of the containing vessel must be attributed, in accordance with modern kinetic conceptions, to the impacts of the ultimate particles of this substance on the boundary walls in the course of their motion, we must in harmony with this assume that the pressure exerted on the walls of the vessel by a molecule dissociated in the above sense will be the same as that exerted by its ions in the free state. If then we could calculate what proportion of the molecules of an electrolyte had undergone dissociation into ions, we could also calculate by van't Hoff's Law the value of the osmotic pressure.

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[1] Clausius, *Pogg. Ann.*, **101**, 347 (1857). Wiedemann, *Elektricität*, **2**, 941.

In a previous communication "Sur la conductibilité galvanique des électrolytes" I have called those molecules, whose ions have independent motion, *active molecules*, and those whose ions are firmly bound together, *inactive molecules.* I have likewise emphasised the probability that at the most extreme dilution all the inactive molecules of an electrolyte are converted into active molecules.[1] On this assumption I will base the calculations made in the sequel. The ratio of the number of active molecules to the total number of molecules, active and inactive, I have called the activity coefficient.[2] The activity coefficient of an electrolyte at infinite dilution is thus assumed to be unity. At smaller dilutions it is less than unity, and, on the principles laid down in the work above cited, is equal to the quotient of the actual molecular conductivity of the solution by the limiting value to which the molecular conductivity of the same solution approaches with increasing dilution. This method of calculation is only applicable if the solutions considered are not too concentrated, *i.e.*, to solutions in which disturbing factors, such as internal friction, etc., can be neglected.

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[1] *Bihang till Kongl. Vet.-Ak. Handlingar*, 8, No. 13, p. 61; No. 14, p. 5 and p. 13 (1884).

[2] [Le coëfficient d'activité d'un électrolyte est le nombre exprimant le rapport du nombre d'iones qu'il y a réelement dans l'électrolyte, au nombre d'iones qui y seraient renfermées, si l'électrolyte était totalement transformé en molécules électrolytiques simples (*loc. cit.*, No. 14, p. 5).]

If the activity coefficient α is known, we can derive from it, as follows, the value of van't Hoff's coefficient i, which is the ratio of the osmotic pressure actually exerted by a substance to the osmotic pressure which it would exert if it consisted entirely of inactive (undissociated) molecules. The coefficient i is obviously equal to the sum of the number of inactive molecules and the number of ions, divided by the total number of molecules, active and inactive. Thus if m is the number of inactive and n the number of active molecules, and if k is the number of ions into which each active molecule is dissociated (*e.g.* for KCl, $k = 2$, viz. K and Cl; for $BaCl_2$ or K_2SO_4, $k = 3$, viz. Ba, Cl and Cl, or K, K and SO_4), then we have

$$i = \frac{m + kn}{m + n}$$

The activity coefficient α is equal to $\frac{n}{m + n}$,

and consequently

$$i = 1 + (k - 1)\alpha.$$

according to which formula the numbers in the last column of the following table have been calculated.

On the other hand the value of i can be calculated by van't Hoff's method from the results of Raoult's experiments on the freezing points of solutions as follows. The depression t of the freezing point of water in degrees centigrade caused by the solution of one gram molecule of the given substance in a litre of water is divided by 18.5, and the values of $i = t/18.5$ thus obtained are tabulated in the second-last column. All numbers given below are calculated on the assumption that 10 grams of the substance were dissolved in 1 litre of water as was actually the case in Raoult's experiments.

In the following table the first two columns give the name and chemical formula of the substance, the third the value of the activity coefficient (Lodge's dissociation-ratio)[1] and the last two the values of i calculated by the two different methods ($i = t/18.5$ and $i = 1 + (k - 1)\alpha$). The substances studied are divided into four main groups: (1) non-conductors, (2) bases, (3) acids, (4) salts.

1.—NON-CONDUCTORS.

Substance.	Formula.	α.	$i = t/18{\cdot}5$.	$i=1+(k-1)\alpha$.
Methyl alcohol . .	CH_3OH	0	0·94	1
Ethyl alcohol . .	C_2H_5OH	0	0·94	1
Butyl alcohol . .	C_4H_9OH	0	0·93	1
Glycerol . . .	$C_3H_5(OH)_3$	0	0·92	1
Mannitol . . .	$C_6H_{14}O_6$	0	0·97	1
Invert sugar . . .	$C_6H_{12}O_6$	0	1·04	1
Cane sugar . . .	$C_{12}H_{22}O_{11}$	0	1·00	1
Phenol	C_6H_5OH	0	0·84	1
Acetone	C_3H_6O	0	0·92	1
Ethyl ether . . .	$(C_2H_5)_2O$	0	0·90	1
Ethyl acetate . . .	$C_4H_8O_2$	0	0·96	1
Acetamide . . .	$C_2H_3ONH_2$	0	0 96	1

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[1] Lodge, On Electrolysis, *Rep. of Brit. Assoc.*, Aberdeen Meeting, 1885, p. 756.

2.—BASES.

Substance.	Formula.	α.	$i = t/18·5$.	$i = 1+(k-1)\alpha$.
Baryta	$Ba(OH)_2$	0·84	2·69	2·67
Strontia	$Sr(OH)_2$	0·86	2·61	2·72
Lime	$Ca(OH)_2$	0·80	2·59	2·59
Lithia	$LiOH$	0·83	2·02	1·83
Soda	$NaOH$	0·88	1·96	1·88
Potash	KOH	0·93	1·91	1·93
Thallium hydroxide .	$TlOH$	0·90	1·79	1·90
Tetramethyl-ammonium hydroxide . .	$N(CH_3)_4OH$	...	1·99	...
Tetraethyl - ammonium hydroxide . .	$N(C_2H_5)_4OH$	0·92	...	1·92
Ammonia . . .	NH_3	0·01	1·03	1·01
Methylamine . . .	CH_3NH_2	0·03	1·00	1·03
Trimethylamine . .	$(CH_3)_3N$	0·03	1·09	1·03
Ethylamine . . .	$C_2H_5NH_2$	0·04	1·00	1·04
Propylamine . . .	$C_3H_7NH_2$	0·04	1·00	1·04
Aniline	$C_6H_5NH_2$	0·00	0·83	1·00

3.—ACIDS.

Hydrochloric . . .	HCl	0·90	1·98	1·90
Hydrobromic . . .	HBr	0·94	2·03	1·94
Hydriodic . . .	HI	0·96	2·03	1·96
Hydrofluosilicic . .	H_2SiF_6	0·75	2·46	1·75
Nitric	HNO_3	0·92	1·94	1·92
Chloric	$HClO_3$	0·91	1·97	1·91
Perchloric . . .	$HClO_4$	0·94	2·09	1·94
Sulphuric . . .	H_2SO_4	0·60	2·06	2·19
Selenic	H_2SeO_4	0·66	2·10	2·31
Phosphoric . . .	H_3PO_4	0·08	2·32	1·24
Sulphurous . . .	H_2SO_3	0·14	1·03	1·28
Hydrogen sulphide .	H_2S	0·00	1·04	1·00
Iodic	HIO_3	0·73	1·30	1·73
Phosphorous . . .	H_3PO_3	0·46	1·29	1·46
Boric	H_3BO_3	0·00	1·11	1·00
Hydrocyanic . . .	HCN	0·00	1·05	1·00
Formic	$HCOOH$	0·03	1·04	1·03
Acetic	CH_3COOH	0·01	1·03	1·01
Butyric	C_3H_7COOH	0·01	1·01	1·01
Oxalic	$(COOH)_2$	0·25	1·25	1·49
Tartaric . . .	$C_4H_6O_6$	0·06	1·05	1·11
Malic	$C_4H_6O_5$	0·04	1·08	1·07
Lactic	$C_3H_6O_3$	0·03	1·01	1·03

4.—SALTS.

Substance.	Formula.	α.	$i = t/18{\cdot}5$.	$i = 1 + (k - 1)\alpha$.
Potassium chloride	KCl	0·86	1·82	1·86
Sodium chloride	$NaCl$	0·82	1·90	1·82
Lithium chloride	$LiCl$	0·75	1·99	1·75
Ammonium chloride	NH_4Cl	0·84	1·88	1·84
Potassium iodide	KI	0·92	1·90	1·92
Potassium bromide	KBr	0·92	1·90	1·92
Potassium cyanide	KCN	0·88	1·74	1·88
Potassium nitrate	KNO_3	0·81	1·67	1·81
Sodium nitrate	$NaNO_3$	0·82	1·82	1·82
Ammonium nitrate	NH_4NO_3	0·81	1·73	1·81
Potassium acetate	$KC_2H_3O_2$	0·83	1·86	1·83
Sodium acetate	$NaC_2H_3O_2$	0·79	1·73	1·79
Potassium formate	$KCHO_2$	0·83	1·90	1·83
Silver nitrate	$AgNO_3$	0·86	1·60	1·86
Potassium chlorate	$KClO_3$	0·83	1·78	1·83
Potassium carbonate	K_2CO_3	0·69	2·26	2·38
Sodium carbonate	Na_2CO_3	0·61	2·18	2·22
Potassium sulphate	K_2SO_4	0·67	2·11	2·33
Sodium sulphate	Na_2SO_4	0·62	1·91	2·24
Ammonium sulphate	$(NH_4)_2SO_4$	0·59	2·00	2·17
Potassium oxalate	$K_2C_2O_4$	0·66	2·43	2·32
Barium chloride	$BaCl_2$	0·77	2·63	2·54
Strontium chloride	$SrCl_2$	0·75	2·76	2·50
Calcium chloride	$CaCl_2$	0·75	2·70	2·50
Cupric chloride	$CuCl_2$	...	2·58	...
Zinc chloride	$ZnCl_2$	0·70	...	2·40
Barium nitrate	$Ba(NO_3)_2$	0·57	2·19	2·13
Strontium nitrate	$Sr(NO_3)_2$	0·62	2·23	2·23
Calcium nitrate	$Ca(NO_3)_2$	0·67	2·02	2·33
Lead nitrate	$Pb(NO_3)_2$	0·54	2·02	2·08
Magnesium sulphate	$MgSO_4$	0·40	1·04	1·40
Ferrous sulphate	$FeSO_4$	0·35	1·00	1·35
Cupric sulphate	$CuSO_4$	0·35	0·97	1·35
Zinc sulphate	$ZnSO_4$	0·38	0·98	1·38
Cupric acetate	$Cu(C_2H_3O_2)_2$	0·33	1·68	1·66
Magnesium chloride	$MgCl_2$	0·70	2·64	2·40
Mercuric chloride	$HgCl_2$	0·03	1·11	1·05
Cadmium iodide	CdI_2	0·28	0·94	1·56
Cadmium nitrate	$Cd(NO_3)_2$	0·73	2·32	2·46
Cadmium sulphate	$CdSO_4$	0·35	0·75	1·35

The last three entries in the second-last column are not, as are all the others, taken from Raoult's[1] work, but from older data of Rüdorff,[2] who used very large quantities of dissolved material, so that those three values cannot lay claim to great accuracy. The values of α are calculated from the data of Kohlrausch,[3] Ostwald[4] (acids and bases), and a few due to Grotrian[5] and Klein.[6] The values calculated from Ostwald's data are by far the most exact, because both the magnitudes involved in α are here easily determined with great accuracy. The error in i calculated from these values of α can scarcely be more than 5 per cent. The values of α and i calculated from Kohlrausch's data are somewhat less certain, chiefly on account of the difficulty of estimating exactly the maximum value of the molecular conductivity. This is still more difficult for α and i calculated from the experimental data of Grotrian and of Klein, which may in unfavourable cases show an error of 10 or 15 per cent. The degree of accuracy of Raoult's numbers is difficult to estimate: judging from the data themselves for very nearly related substances errors of 5 per cent. or even somewhat more are not improbable.

It should be noted that in the above tables there have been included for the sake of completeness *all* substances for which a moderately accurate calculation of i by the two methods has been found possible. When conductivity data for a substance were wanting, *e.g.*, cupric chloride and tetramethylammonium hydroxide, for purposes of comparison the calculation was made from the data for a nearly related substance (zinc chloride and tetra-ethylammonium hydroxide) whose electrical properties could not be notably different from those of the substance in question.

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[1] Raoult, *Ann. de Ch. et de Phys.* [5] **28**, 133 (1883); [6] **2**, 66, 99, 115 (1884); [6] **4**, 401 (1885).

[2] Rüdorff, cited in Ostwald's *Lehrbuch der allg. Chemie* [1st Edition], **1**, 414.

[3] Kohlrausch, *Wied. Ann.*, **6**, 1 and 145 (1879); **26**, 161 (1885).

[4] Ostwald, *Journ. f. pr. Ch.* [2] **32**, 300 (1885); [2] **33**, 352 (1886); *Zeit. physikal. Chem.*, **1**, 74 and 97 (1887).

[5] Grotrian, *Wied. Ann.*, **18**, 177 (1883)

[6] Klein, *Wied. Ann.*, **27**, 151 (1886).

From the values of *i* which exhibit a very great difference between the two methods of calculation, that for H_2SiF_6 should probably at the outset be excluded, for Ostwald has shown that in all probability this acid in aqueous solution partially decomposes into 6HF and SiO_2, which would explain the high value of *i* found by Raoult's method.[1]

There is one circumstance which to a small extent tends to invalidate the comparison between the last two columns, namely, that the values in strictness hold good for different temperatures. The values in the second-last column are all for temperatures differing little from 0° C. as they have been derived from experiments on slight lowerings of the freezing point of water. On the other hand the values in the last column for acids and bases (Ostwald's experiments) were obtained at 25° C., the others at 18° C. The figures in the last column for non-conductors are of course also valid for 0° C., since these substances at this temperature also contain no appreciable quantity of dissociated (active) molecules.

There appears nevertheless on a comparison of the numbers in the last two columns a very marked parallelism between them.[2] This shows a posteriori that in all probability the assumptions on which I have based the calculation are in the main correct. These assumptions were:—

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[1] [Compare, however, E. Baur, *Zeit. physikal. Chem.*, 48, 483 (1904).]

[2] For some salts forming definite exceptions, see below, p. 53.

(1) That van't Hoff's law holds good not merely for the *majority* but for *all* substances, including those formerly regarded as exceptions (electrolytes in aqueous solution).

(2) That every electrolyte in aqueous solution consists in part of molecules electrolytically and chemically active and in part of inactive molecules which, however, on dilution change into active molecules, so that at infinite dilution only active molecules are present.

The objections which may probably be urged from the chemical side, are in the main the same as those raised against Clausius' hypothesis, and these I have already endeavoured to show are completely untenable.[1] A repetition of these objections may therefore be regarded as superfluous. I will emphasise only one point. Although the dissolved substance exerts on the walls of the vessel an osmotic pressure precisely as if it were partly dissociated into ions, yet the dissociation here in question is not quite the same as that, for instance, which is shown by the decomposition of an ammonium salt at a high temperature. In the first case the products of dissociation (the ions) have very large electrical charges of opposite sign, and thus are subject to certain conditions (the incompressibility of electricity), from which it follows that the ions cannot without a great expenditure of energy be separated from each other in any marked degree.[2] In ordinary dissociation, on the other hand, where such conditions do not occur, the products of dissociation can generally be separated from each other.

These two assumptions are of the most far-reaching significance, not only from the theoretical point of view, which will receive discussion below, but also in the highest degree from the practical standpoint. If it can be shown—and I have endeavoured to make it highly probable—that the law of van't Hoff is universally applicable, then the chemist has at hand an extraordinarily convenient means of determining the molecular weight of any substance soluble in a liquid.[1]

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[1] *Loc. cit.*, No. 14, pp. 6 and 31.

[2] *Ibid.*, No. 14, p. 8.

I may also draw attention to the fact that the above equation (1) gives the connection between the two magnitudes i and α which play the chief parts in the two theories recently developed by van't Hoff and by myself.

In the above calculation of i I have tacitly assumed that the inactive molecules exist in the solution as simple molecules and not united to form larger molecular complexes. The results of this calculation (*i.e.*, the figures in the last column) compared with the results of direct observation (the figures in the second-last column) show that in general the supposition is completely justified. Were it not so, the numbers in the second-last column would be smaller than those of the last. Exceptions in which this is without doubt the case are found in the sulphates of the magnesium series ($MgSO_4$, $FeSO_4$, $CuSO_4$, $ZnSO_4$, and $CdSO_4$) and also in cadmium iodide. To explain these we may assume that the inactive molecules of these salts in reality combine with each other. Hittorf[2] was led to make this assumption for CdI_2 by the great change in the transport ratio; and if we look more closely at his table we find an unusually large alteration of the ratio for the three sulphates of the above series which he investigated, namely, $MgSO_4$, $CuSO_4$, and $ZnSO_4$. It is thus quite probable that this explanation is applicable to the salts mentioned. For the other salts we must assume that double molecules are only present in very small proportions. It remains now to indicate in a few words the grounds which have led previous authors to the assumption of a general occurrence of complex molecules in solutions.

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[1] This method has already been applied. Compare Raoult, *Ann. d. Ch. et d. Phys.* [6] 8, 317 (1886). Games Paternò and Nasini, *Berichte d. deut. chem. Ges.*, 1886, p. 2527.

[2] Hittorf, *Pogg. Ann.*, **106**, 547 and 551 (1859); Wiedemann, *Elektricität*, **2**, 584.

Since, generally speaking, substances in the gaseous state consist of simple molecules, in accordance with Avogadro's Law, and since in the neighbourhood of the condensation point a small increase in density frequently occurs, which indicates a combination of these simple molecules, it was thought that in the change from the gaseous to the liquid state there would be a much greater amount of combination, that is, it was assumed that liquid molecules are in general not simple. I do not mean here to challenge the accuracy of this conclusion, but there is a great difference when the liquid considered is dissolved in another (*e.g.* HCl in water). For if we assume that on dilution the originally inactive molecules are transformed into active molecules, the ions being to a certain extent separated from each other, a process which is naturally accompanied by a great expenditure of energy, there is no difficulty in also making the assumption that the molecular complexes on mixing with water are likewise for the most part broken up, no great amount of work being thereby required. The fact that heat is absorbed on dilution has also been regarded as affording evidence for the existence of molecular complexes,[1] but, as we have seen, this might equally well be ascribed to the activation of the molecules. Some chemists, too, for the purpose of maintaining constant valency, assume the existence of molecular complexes in which the superfluous valencies satisfy each other.[2] The doctrine of constant valency is, however, so much disputed that one can scarcely use it as a basis for deduction. The conclusion arrived at in this way, that potassium chloride has the formula $(KCl)_3$, Lothar Meyer endeavours to support by drawing attention to the circumstance that KCl is much less volatile than $HgCl_2$ although it has a much smaller molecular weight. Apart altogether from the insecure basis on which such an argument is founded, the conclusion evidently applies only to pure substances, not to solutions. There are several other reasons adduced by Lothar Meyer for the existence of molecular complexes, for instance, that NaCl diffuses more slowly than HCl,[3] which, however, is to be attributed to the probably greater friction (according to electrolytic determinations) of Na than H against water. It is sufficient, however, to quote Meyer's own words: "However incomplete and uncertain all these various indications of methods for determining molecular weights in the liquid state may still be, yet they permit us to hope that in future it will be possible to determine the magnitude of the molecules. . . ."[4] van't Hoff's Law, however, now gives quite definite indications that in the vast majority of cases the number of molecular complexes in aqueous solution is negligible, although in a few cases, which are precisely those formerly used in support of the assumption of molecular complexes,[1] their existence is confirmed. It is not of course denied that such molecular complexes may exist in the case of other salts, particularly in concentrated solutions; but in solutions of the degree of dilution which Raoult examined they exist in general in such small quantity that they may be neglected in the above calculations without appreciable error.

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[1] Ostwald, *Lehrb. d. allg. Chem.* [1st edition], **1**, 811. L. Meyer, *Moderne Theorien der Chemie*, p. 319 (1880).

[2] L. Meyer, *loc. cit.*, p. 360.

[3] *Ibid.*, p. 316.

[4] *Ibid.*, p. 321. van't Hoff's Law makes this possible, *vide supra*.

Most of the properties of dilute salt solutions are of a so-called additive character. In other words, the numerical values of the properties may be regarded as the sum of the properties of the parts of the solution, *i.e.*, of the solvent and of the parts of the dissolved molecules, which in fact coincide with the ions. For example, the conductivity of a salt solution may be regarded as the sum of the conductivities of the solvent (generally zero), of the positive ion, and of the negative ion. In most cases this can be tested by comparing two salts (*e.g.* of K and Na) of one acid (*e.g.* HCl) with the corresponding salts of the same metals (K and Na) and another acid (*e.g.* HNO_3). Then the property of the first salt (KCl) minus the property of the second (NaCl) is equal to the property of the third salt (KNO_3) minus the property of the fourth ($NaNO_3$). This holds good in most cases for several properties, *e.g.* conductivity, lowering of the freezing point, refraction equivalent, heat of neutralisation, etc., which we shall briefly consider in the sequel, and finds its explanation in the almost complete dissociation of the great majority of salts into their ions. If a salt in aqueous solution is completely split into its ions, it follows naturally that the properties of this salt may in the main be expressed as the sum of the properties of the ions, since the ions are for the most part independent of each other, so that each ion has a characteristic value for the property, whatever be the oppositely charged ion with which it is associated. In the solutions actually investigated complete dissociation is probably never reached, and the above deduction is therefore not strictly accurate, but if we consider salts which are 80 or 90 per cent. dissociated, as are almost without exception the salts of strong bases with strong acids, we shall in general commit no very great errors by calculating the values of the properties on the assumption that the salts are completely decomposed into their ions. According to the foregoing table this applies also to the strong bases and acids $Ba(OH)_2$, $Sr(OH)_2$, $Ca(OH)_2$, LiOH, NaOH, KOH, TlOH and HCl, HBr, HI, HNO_3, $HClO_3$ and $HClO_4$. But there is another group of substances which have hitherto in most investigations played a subordinate part and are far removed from complete dissociation, even in dilute solution, as, for example, according to the table, $HgCl_2$ (and other Hg salts), CdI_2, $CdSO_4$, $FeSO_4$, $MgSO_4$, $CuSO_4$ and $Cu(C_2H_3O_2)_2$, the weak bases and acids, such as NH_3 and the various amines, H_3PO_4, H_2S, H_3BO_3, HCN, formic, acetic, butyric, tartaric, malic and lactic acids. The properties of these substances will not, as a rule, be of the same (additive) nature as those previously considered, as we shall find completely confirmed in the sequel. There exists naturally a number of transitional compounds between these two groups, as may be seen from the table. It should be mentioned here that in consideration of the almost universal occurrence of additive properties in substances of the first group, which are those by far the most frequently studied, several investigators have been led to the assumption of a certain complete dissociation of salts into their ions.[1] Since, however, from the purely chemical point of view no reason could be found why salt molecules should decompose in a perfectly definite way (into their ions), since in addition, for reasons which need not be discussed here, chemists have contested as long as possible the existence of unsaturated radicals (under which rubric ions are included), and since the foundations of such an assumption are somewhat uncertain,[2] the hypothesis of a complete dissociation has till now found little favour. The above table shows also that the reluctance of chemists to accept the complete dissociation demanded is not without a certain justification, inasmuch as at the dilutions actually employed the dissociation is never complete, being indeed for a large number of electrolytes (those of the second group) relatively insignificant.

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[1] Kohlrausch, *Wied. Ann.*, 6, p. 167 (1879).

From these observations we proceed to the special cases in which additive properties occur.

1. **Heat of neutralisation in dilute solutions.**—In the neutralisation of an acid by a base the energies of these two substances are disengaged as heat, but at the same time there is absorbed a certain quantity of heat arising from the energies of the water and salt (ions) which have been formed. We indicate by curved brackets the energies of the substances, for which it is immaterial so far as the deduction is concerned whether they occur as ions or not, and by square brackets those of the ions, the energies taken for them being always those in dilute solution. For example, on the provisional assumption of complete dissociation of the salts, we have for the neutralisation of NaOH by $\frac{1}{2}H_2SO_4$ (1)

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[1] Valson, *Compt. rend.*, **73**, 441 (1871); **74**, 103 (1872). Favre and Valson, *Compt. rend.*, **75**, 1000 (1872). Raoult, *Ann. d. Chim. et d. Phys.* [6] **4**, 426.

[2] For Raoult's different hypotheses, compare *loc. cit.*, p. 401.

and HCl (2) and of KOH by $\frac{1}{2}H_2SO_4$ (3) and HCl (4) all in equivalent quantities, liberation of the following amounts of heat:—

$$(NaOH) + \tfrac{1}{2}(H_2SO_4) - (H_2O) - [Na] - \tfrac{1}{2}[SO_4] \quad (1)$$
$$(NaOH) + (HCl) - (H_2O) - [Na] - [Cl] \quad (2)$$
$$(KOH) + \tfrac{1}{2}(H_2SO_4) - (H_2O) - [K] - \tfrac{1}{2}[SO_4] \quad (3)$$
$$(KOH) + (HCl) - (H_2O) - [K] - [Cl] \quad (4)$$

We have obviously $(1) - (2) = (3) - (4)$ if we assume complete dissociation of the salts. As indicated above, this is approximately true for the instances which actually occur. It is all the more the case because the salts which are furthest from complete dissociation—here Na_2SO_4 and K_2SO_4—are dissociated approximately to the same extent, whereby the error occurring in the two members of the last equation is approximately the same, a circumstance which determines the occurrence of additive properties somewhat more frequently than one might expect. The following short table (p. 60) shows that on the neutralisation of strong bases and strong acids the additive properties are clearly apparent. For salts of weak bases with weak acids this is no longer the case, because they are probably partially decomposed by the water.

The numbers in brackets represent the difference between the heat evolution of the salt considered and that of the corresponding chloride. It will be seen if we neglect the last column that they are in each vertical column approximately constant. This is closely connected with the thermo-neutrality of salts; but since I have on a previous occasion treated this subject more particularly and emphasised the close connection with the Williamson-Clausius hypothesis,[1] I need not here enter into any detailed analysis.

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[1] *Loc. cit.*, No. 14, p. 67.

Heats of Formation of some Salts in Dilute Solution.
(*From the Data of Thomsen and Berthelot.*)

	HCl, HBr, or HI.	HNO_3.	$C_2H_4O_2$.	CH_2O_2.
NaOH	13·7	13·7 (0·0)	13·3 (−0·4)	13·4 (−0·3)
KOH	13·7	13·8 (+0·1)	13·3 (−0·4)	13·4 (−0·3)
NH_3	12·4	12·5 (+0·1)	12·0 (−0·4)	11·9 (−0·5)
$\frac{1}{2}$ $Ca(OH)_2$	14·0	13·9 (−0·1)	13·4 (−0·6)	13·5 (−0·5)
$\frac{1}{2}$ $Ba(OH)_2$	13·8	13·9 (+0·1)	13·4 (−0·4)	13·5 (−0·3)
$\frac{1}{2}$ $Sr(OH)_2$	14·1	13·9 (−0·2)	13·3 (−0·8)	13·5 (−0·6)

	$\frac{1}{2}$ $(CO_2H)_2$.	$\frac{1}{2}$ H_2SO_4.	$\frac{1}{2}$ H_2S.	HCN.	$\frac{1}{2}$ CO_2.
NaOH	14·3 (+0·6)	15·8 (+2·1)	3·8 (−9·9)	2·9 (−10·8)	10·2 (−3·5)
KOH	14·3 (+0·6)	15·7 (+2·0)	3·8 (−9·9)	3·0 (−10·7)	10·1 (−3·6)
NH_3	12·7 (+0·3)	14·5 (+2·0)	3·1 (−9·3)	1·3 (−11·1)	5·3 (−7·1)
$Ca(OH)_2$	...	...	3·9 (−10·1)	...	...

2. **Specific volume and specific gravity of dilute solutions.**—If we add to a litre of water a small quantity of salt, whose ions may be regarded as completely independent, the volume is thereby changed. If x is the quantity of the one ion added and y that of the other ion, the volume as a first approximation will be $1 + ax + by$ litres where a and b are constants. Since the ions are dissociated from each other, the constant a of one ion will be independent of the nature of the other ion. In the same way the weight is $1 + cx + dy$ kilos where c and d are two other constants characteristic of the ions. Thus, for small quantities of x and y, the specific gravity is given by the formula

$$1 + (c - a)x + (b - d)y$$

where $(c - a)$ and $(b - d)$ are characteristic constants for the two ions. The specific gravity is thus for dilute solutions an additive property as Valson found.[1] But, according to Ostwald, "specific gravity is not a property to be used for the representation of stoichiometric laws,"[2] so we need not enter on a closer discussion of these results. The determination of the constants *a* and *b*, etc., would be promising, but so far has not been carried out.

In close connection with these phenomena is the change of volume on neutralisation. From similar considerations to those put forward for heat of neutralisation, it may be shown that the change of volume on neutralisation is an additive property. It is evident from the above table that all the K, Na, and NH_4 salts investigated are almost completely dissociated, as is still clearer from the later work of Ostwald, so that we may expect very good agreement for these salts. The differences in the change of volume on the formation of the corresponding salts of nineteen different acids appear as practically constant quantities.[3] Since the bases which form salts of the second group have not been investigated, no exceptions are yet known.

3. **Specific refraction of solutions.**—In mixtures of various substances the expression $P.\frac{n-1}{d}$ for the different components (where n is the refractive index, d the density and P the weight) may be summed to give the corresponding magnitude for the mixture. Consequently this magnitude, the refraction equivalent, must be an additive property for dissociated salts also. That this is in fact the case has been clearly shown by the researches of Gladstone. In this instance the

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[1] Valson, *Compt. rend.*, **73**, 441 (1871). Ostwald, *Lehrbuch* [1st edition], **1**, 384.

[2] Ostwald, *loc. cit.*, p. 386.

[3] Ostwald, *loc. cit.*, p. 388.

potassium and sodium salts as well as the acids themselves have been investigated. The following table of molecular refraction equivalents has been extracted from Ostwald's *Lehrbuch*.[1]

	Potassium.	Sodium.	Hydrogen.	K – Na.	K – H.
Chloride . .	18·44	15·11	14·44	3·3	4·0
Bromide . .	25·34	21·70	20·63	3·6	4·7
Iodide . .	35·33	31·59	31·17	3·7	4·2
Nitrate . .	21·80	18·66	17·24	3·1	4·5
Sulphate .	30·55	...	22·45	...	2 × 4·1
Hydroxide .	12·82	9·21	5·95	3·6	6·8
Formate . .	19·93	16·03	13·40	3·9	6·5
Acetate . .	27·65	24·05	21·20	3·6	6·5
Tartrate . .	57·60	50·39	45·18	2 × 3·6	2 × 6·2

We see that the difference K – Na is everywhere much the same, as was to be expected from what we know of the degree of dissociation of the K and Na salts; the same also holds good for the difference K – H as long as the strong (dissociated) acids are considered. On the other hand the substances of the second group (the feebly dissociated acids) show quite different behaviour, the difference K – H being here much greater than for the first group.

4. **Capillarity.**—Valson[2] believed he had found additive properties in the capillary phenomena shown by salt solutions. We need not, however, consider the matter here, since it may be traced back to the circumstance that specific gravity is an additive property as has been shown above.

5. **Conductivity.**—The credit of a great step in the development of the theory of electrolysis is due

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[1] Ostwald, *Lehrbuch* [1st edition], **1**, 443.

[2] Valson, *Compt. rend.*, **74**, 103 (1872). Ostwald, *loc. cit.*, p. 492.

to F. Kohlrausch, who showed that conductivity is an additive property.[1] As we have already indicated in what sense this is to be understood, we may pass directly to the experimental data. For dilute solutions Kohlrausch gives in the memoir cited the following values:—

$K = 48$, $NH_4 = 47$, $Na = 31$, $Li = 21$, $Ag = 40$,
$H = 278$, $Cl = 49$, $Br = 53$, $I = 53$, $CN = 50$,
$OH = 141$, $F = 30$, $NO_3 = 46$, $ClO_3 = 40$,
$C_2H_3O_2 = 23$, $\frac{1}{2}Ba = 29$, $\frac{1}{2}Sr = 28$, $\frac{1}{2}Ca = 26$,
$\frac{1}{2}Mg = 23$, $\frac{1}{2}Zn = 20$, $\frac{1}{2}Cu = 29$.

These values, however, only hold good for the most highly dissociated substances (salts of monobasic acids, and the strong acids and bases). For the somewhat less dissociated sulphates and carbonates of the univalent metals (compare the previous table) he obtained much smaller values:

$K = 40$, $NH_4 = 37$, $Na = 22$, $Li = 11$, $Ag = 32$.
$H = 166$, $\frac{1}{2}SO_4 = 40$, $\frac{1}{2}CO_3 = 36$,

and for the least dissociated sulphates (those of the metals of the magnesium series) he obtained the still smaller values

$\frac{1}{2}Mg = 14$, $\frac{1}{2}Zn = 12$, $\frac{1}{2}Cu = 12$, $\frac{1}{2}SO_4 = 22$.

It is thus evident that Kohlrausch's Law is only applicable to the most highly dissociated salts, the less dissociated salts giving very different values. Since, however, the number of active molecules increases with rising dilution, so that at the most extreme dilution all salts have decomposed into only active (dissociated) molecules, it was to be expected that at high dilutions the salts would behave more regularly. I also showed from some examples that "too much importance should not be attributed to the anomalies of the salts (acetates and sulphates) of the metals of the magnesium series, since these anomalies disappear at high dilutions."[1] I likewise thought it was possible to carry out consistently the idea that conductivity is an additive property,[2] and attributed to the conductivity of hydrogen in all acids (even those which conduct worst of all, though their behaviour was *prima facie* at variance with this idea) a value completely independent of the nature of the acid, which could only be done with the help of the activity concept. The correctness of this view is more evident still from the later researches of Kohlrausch[3] and Ostwald.[4] In his last work on this subject Ostwald[4] tried to prove that without the assistance of the activity concept it is possible to apply generally the hypothesis that conductivity is an additive property, and this succeeds very well with the sodium, potassium, and lithium salts investigated by him, because these are as a rule very near complete dissociation, especially at very high dilution. The conclusion is still further supported by the fact that analogous salts of univalent metals, as being very closely related to each other, are at the same concentration about equally dissociated. If, however, we consider salts of less nearly related metals, we should arrive at quite different conclusions, as previous investigators clearly make evident. It is stated by Ostwald himself[5] that Kohlrausch's Law is not without modification applicable to acids, introduction of the activity concept being necessary if it is to be carried through systematically. A closer investigation of copper acetate would lead to considerable difficulties, and still more would this be the case with mercury salts, for according to Grotrian's[1] investigations it appears as if these, even at the most extreme dilutions, yield a conductivity which is only a small fraction of that deduced from the law. It seems indeed that not all salts of the univalent metals are subject to this law, for Bouty[2] has found that potassium stibiotartrate, even in 0.001-normal solution, has only a fifth of the conducting power of KCl; according to Kohlrausch's Law it should have at least half. When, however, we introduce the concept of activity the law of Kohlrausch can be completely carried through, for in the above table the values of *i* calculated from this law by means of the activity concept show, even in the case of weak bases and acids as well as for $HgCl_2$ and $Cu(C_2H_3O_2)_2$, good agreement with the values of *i* calculated from Raoult's experiments.

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[1] Kohlrausch, *Wied. Ann.*, 6, 167 (1879); Wiedemann, *Elektricität*, **1**, 610; **2**, 955.

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[1] *Loc. cit.*, No. 13, p. 41. [2] *Loc. cit.*, No. 14, p. 12.

[3] Kohlrausch, *Wied. Ann.*, **26**, 215 and 216 (1885).

[4] Ostwald, *Zeit. physik. Chem.*, **1**, 74 and 97 (1887).

[5] *Loc. cit.*, p. 79.

6. **Lowering of the freezing-point.**—In one of his papers Raoult[3] indicates that the lowering of the freezing-point of water can be regarded as an additive property, as would naturally be the case according to our conception for the more dissociated salts in dilute solution. He gives the following values for the effect of the ions:—

Group	I. Univalent electronegative ions (radicals) (Cl, Br, OH, NO_3, etc.) . . .	20
,,	II. Bivalent electronegative ions (radicals) (SO_4, CrO_4, etc.)	11

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[1] Grotrian, *Wied. Ann.*, 18, 177 (1883).

[2] Bouty, *Ann. d. Chim. et d. Phys.* [6] 3, 472 (1884).

[3] Raoult, *Ibid.*, [6] 4, 616 (1885).

Group III. Univalent electropositive ions (radicals) (H, K, Na, NH_4, etc.) . . . 15

„ IV. Bi- or multivalent[1] electropositive ions (radicals) (Ba, Mg, Al_2, etc.) . . . 8

There are, however, very many exceptions, marked by unusually small dissociation, even in the most dilute solutions, as the following table shows:—

	Calculated.	Found.
Weak acids . . .	35	19·0
Cupric acetate . . .	48	31·1
Potassium stibiotartrate .	41	18·4
Mercuric chloride . .	48	20·4
Lead acetate . . .	48	22·2
Aluminium acetate . .	128	84·0
Ferric acetate . . .	128	58·1
Platinic chloride . . .	88	29·0

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[1] According to the ideas developed above, all ions should have the same value 18·5. Raoult has artificially forced into the general law of the additive nature of freezing-point depressions, ions of the less dissociated substances like $MgSO_4$ by giving them much smaller values, namely, 8 and 11. The possibility of consistently attributing small values to the multivalent ions depends on the circumstance that in general the dissociation of salts is less as the valency of their ions is greater, as I have previously emphasised (*loc. cit.*, No. 13, p. 69; No. 14, p. 5): "The inactivity (complexity) of a salt solution is the greater, the more easily the constituents of the salt (acid and base) form double compounds (acid or basic salts)." This result is completely supported by the later work of Ostwald (*Zeit. physikal. Chem.*, **1**, pp. 105 to 109). It is evident that if the correct value of 18.5 is attributed to the multivalent ions, the salts compounded from them would form pronounced exceptions. (Probably a similar view might rightly be adopted for other additive properties.) Thus, although Raoult by artificial devices has forced these little dissociated salts into the framework of his law, he has not succeeded with all salts, as is shown in the text.

From measurements of electrical conductivity we know that the molecules of the first four substances are very little dissociated; the others are closely related to them, so that we may expect the same to be true of them also, although their electrolytic properties have not yet been studied. From our point of view all these substances, in this case as in those previously discussed, are not to be regarded as exceptions, but as obeying precisely the same laws as those other substances previously regarded as normal.

In close connection with the lowering of the freezing-point there are several other properties of salt solutions which, as Guldberg[1] and van't Hoff[2] have shown, are proportional to the freezing-point depression. All these properties (lowering of vapour pressure, osmotic pressure, isotonic coefficient) are then to be looked upon as additive, as has indeed been shown by de Vries[3] for the isotonic coefficient. Since, however, all these properties can be deduced from the freezing-point depression, I do not think it necessary to discuss their details in this paper.

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[1] Guldberg, *Compt. rend.*, **70**, 1349 (1870).

[2] van't Hoff, *loc. cit.*, p. 20.

[3] de Vries, "Eine Methode zur Analyse der Turgorkraft," *Pringsheims Jahrbücher*, **14**, 579 (1884); van't Hoff, *loc. cit.*, p. 26.

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PROUT'S HYPOTHESIS

PAPERS BY
WILLIAM PROUT, M.D.
(1815-16)
J. S. STAS
(1860)
AND C. MARIGNAC
(1860)

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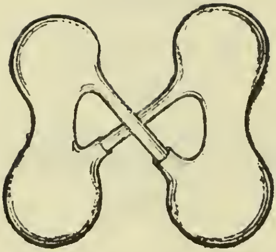

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PREFACE

THE change in view regarding Prout's Hypothesis brought about by twentieth century physical and physico-chemical investigation affords a suitable occasion for reproducing in this reprint the original papers of Prout and, along with them, two of the most important of the papers dealing with determinations made during the nineteenth century in connection with the hypothesis. The papers by Stas and Marignac sufficiently characterise the aspect that the matter had assumed in 1860 and still presented more than forty years later. Certain details connected with the early history of the hypothesis, together with a number of points correlating the hypothesis with recent advances, are set forth in the Historical Introduction.

October 1932.

PROUT'S HYPOTHESIS

HISTORICAL INTRODUCTION

THE enunciation in a rather indefinite and tentative manner of the conception which has long been familiar to chemists as "Prout's Hypothesis" and which suggested that the atomic weights of the other elements were multiples by whole numbers of that of hydrogen, dates from the appearance of two papers—both written by Prout but originally published anonymously—contributed in 1815 and 1816 to Thomson's Annals of Philosophy. The texts of these papers, together with fac-simile copies of the Tables which were included in them, are reproduced at pp. 25 and 38, respectively, of this reprint.

The passing allusion, in the closing paragraph of the second of these papers, to the opinion that we may almost consider the primordial substance of the ancients to be realised in hydrogen, as one that was not at that time new, warrants the assumption that vague foreshadowings of it had presented themselves to the minds of previous thinkers. Indeed such foreshadowings may possibly be recognised as existing, in more or less hazy form, in certain passages in the writings of Dalton, Davy, and Thomas Thomson.

Thomson, in the following passage which occurs in his "Account of the Improvements in Physical Science during the Year 1815," indicates the importance which he attaches to the relation referred to in the first of the anonymous papers by Prout mentioned above:—

> In the historical introduction to the *Annals of Philosophy* for last year, an account was given of the general principles of the atomic theory. An account was also given of a modification of that theory by Berzelius, in which he substitutes volumes for atoms; supposing all substances in the first place to be in the gaseous state. A very important paper was published in a late number of the *Annals of Philosophy* on this subject. Though the paper in question is anonymous, several circumstances enable me to fix with considerable certainty on the author; but as he chuses to remain for the present concealed, I do not consider myself as at liberty to mention his name. The title of the paper is On the Relation between the Specific Gravities of Bodies in their Gaseous State, and the Weight of their Atoms (*Annals of Philosophy*, vol. vi. p. 321). By pointing out this relation, he shows that the two modes of viewing the atomic theory come in fact to the same thing.*

A few months later, in a paper entitled "Some Observations on the Relations between the Specific Gravity of Gaseous Bodies and the Weights of their Atoms,"† Thomson indicated that Dr Prout‡ was the author of the previously anonymous papers.

Thomson was, from the outset, a warm supporter of the atomic theory as advanced by Dalton in the early years of the nineteenth century and, in 1815, had himself already been engaged for several years in making atomic weight determinations. He took up with much zeal and enthusiasm the idea announced in Prout's papers and soon published various communications on atomic weights in support of it. Moreover he devoted himself for a number of years to a scheme of experimental work designed to establish its validity and embodied the results of this work in two comprehensive volumes which he published in 1825 under the title: "An Attempt to Establish the First Principles of Chemistry by Experiment." Strictures regarding the methods by which Thomson attained his results and statements as to inaccuracies in the results themselves were made by Berzelius who, prior to 1815, had been engaged for several years in elaborate quantitative analytical work on the composition of numerous salts and on the determination of atomic weights. As far as the attitude of Berzelius towards Prout's idea is concerned, he simply continued his own investigations without paying much regard to it, since to begin with, it did not commend itself favourably to him, and, later, he expressed himself as definitely opposed to it.

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* Annals of Philosophy, **7** (1816), 17. † *Ibid.*, **7** (1816), 343.

‡ Dr William Prout, born in Horton, Gloucestershire, in 1785, studied medicine in Edinburgh where he obtained the degree of M.D. in 1811. He carried on medical practice in London and contributed numerous papers, mostly upon medical subjects, to various journals. He was the discoverer of the presence of free hydrochloric acid in the gastric fluid.

A matter of considerable historical interest which appears to have attracted comparatively little attention is the fact that shortly after the appearance of Prout's first paper, Professor J. L. G. Meinecke, of Halle, published several lengthy papers on Chemical Measurements in which he made more or less definite reference to the circumstance that the numbers representing the relative weights of the "portions" (Antheile), as he called them, of the various elements were multiples by whole numbers of that of hydrogen. Meinecke is not usually named in this connection by the historians of chemistry or by writers on Prout's Hypothesis, but he is mentioned, along with Prout, by Thorpe in his Graham Lecture to the Philosophical Society of Glasgow, in 1887,* while Ostwald in his *Lehrbuch* † deals with "The Hypothesis of Prout and Meinecke." In the earliest of his papers on chemical measurements, published in 1816, Meinecke, when dealing with the adoption of a "round number" to represent the weight of the "portion" of each element, explained how he chose a number which was based upon the results obtained, usually, by several different observers although it was not necessarily the average deduced from these results. By a round number Meinecke understood one which arose either by a simple sub-division of the value for oxygen or was divisible by the number for hydrogen, and he mentioned that the number adopted for carbon (0·750 with oxygen = 1) was three fourths of that of oxygen and twelve times that of hydrogen. In connection with the adoption of a particular weight for each element he stated that the guiding principle was not to deduce the value from any single compound of a substance but from its various compounds and, in the case of divergent analyses, not to choose the mean but to follow the substance through its numerous compounds in order to ascertain definitely the figure by which its value could be most accurately expressed. He writes:—

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* Essays in Historical Chemistry (1894), 228.

† Lehrbuch der allgemeinen Chemie, 2nd Edition (1891), I, 126, 127.

> These comparative calculations led us to adopt particular round numbers, not so much for the simplification of calculation as because we were satisfied from the divergences in the analyses made by the most accurate chemists, as well as from our own experience, that for the present nothing more could be given than approximations in round numbers. . . . With regard to most of the numbers here noted, we are in complete agreement with the most distinguished chemists and in the remaining numbers we diverge but little. This agreement tells in favour of the assumption of definite round numbers even if the surprising simplicity which the chemist finds still more plainly with every new discovery amongst the most complicated compounds should not remind him that a simple relationship to one another (which we call round numbers) must exist amongst the elements themselves.*

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* Journal der Pharmacie (Trommsdorff), 25 (1816), 2nd Part, 72, 200-202.

The figures which he adopts in text and tables for the values of the "portions" of other elements, as compared with that of hydrogen, are all whole numbers.

In a second paper, also published in 1816, Meinecke dealt more fully with the subject of round numbers and was quite definite with respect to them. He expressly stated there that "according to Dalton, all stoichiometric magnitudes are multiples by whole numbers of the value of hydrogen" and added that "even although the atomistic conceptions which form the basis for that proposition are not accepted, it must still be regarded as remarkable that most stoichiometric values are exactly, while all are nearly, divisible by the value for hydrogen." * He published further papers in 1818 and 1819 in which he returned to the subject of the simple relation of the stoichiometric values of the other elements to that of hydrogen. † He also published in book form, in 1817, the second part of a work on Chemical Measurement. ‡ Prout's paper was not referred to in any of these publications and the omission, considered in connection with his subsequent attitude in the question of priority (see below), awakens the impression that Meinecke was disappointed at having been narrowly anticipated by Prout in stating the generalisation advanced by the latter.

In a volume on Stoichiometry published under date 1819 by Carl G. C. Bischof, Docent at Erlangen till

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* Annalen der Physik (Gilbert), **24** (1816), 162.

† Journal für Chemie und Physik (Schweigger), **22** (1818), 138; Isis von Oken (1818), 1574; Neues Journal der Pharmacie, **3**, Part 2 (1819), 478.

‡ Erläuterungen zur chemischen Messkunst: Halle, 1817. The First Part of this book was published in 1815, but this did not contain any idea suggestive of an anticipation of the generalisation advanced in that year by Prout.

1819, thereafter Professor of Chemistry at Bonn, the author gives a lengthy résumé of the Prout-Meinecke publications and a commentary. From the latter it is evident that there was no doubt in Bischof's mind as to Prout's priority. He says, § 54, p. 164:—

> Later Meinecke used one of the results following from Prout's investigations for the exact determination of the specific gravities of elastic fluids.

and in a foot-note to p. 173 he says:—

> The results of his determinations are for the rest exactly the same as we found in the . . . Tables of Prout and Thomson. . . . But Meinecke has forgotten to cite Prout's paper.

Referring to Meinecke's 1815 volume he says, § 55, p. 173:—

> Simultaneously with Prout, Meinecke treated the same subject from another point of view:

and referring to his 1817 volume he proceeds (p. 182):—

> In the second part of his Chemical Measurement . . . the author reverts rather to Richter's presentation of the question. He determines the combining ratios of the substances and gives very complete tables. He is guided here by the highly important fact, as he calls it, that the combining ratio of all substances is so nearly a multiple of that of hydrogen that if the numbers found from the various analyses are replaced by exact multiples of the value for hydrogen, this multiple of hydrogen deviates less from the mean of the experimental magnitudes than most of these magnitudes [from each other?]. He flatters himself that he has found in this way an important aid to the very exact determination of combining numbers.
>
> But we must remember that it is really Prout who hit upon this agreement (see above, § 54). However, we cannot value this quite so highly; for the combining number of hydrogen is small in comparison with most of the others. The ratio therefore in which these stand to it is so great that half its value can easily fall within the limits of possible error of observation, and consequently [integral] multiples can easily be found.

In a paper which he published in 1819,* Meinecke took exception to the observation by Bischof that he had "forgotten to cite Prout's paper," † and asserted that "Dalton assumed long ago that all stoichiometric values were divisible by that of hydrogen, without, however, calculating these values accurately by the aid of available analyses." This assertion regarding Dalton deserves examination. No *direct* reference to any such assumption as that stated by Meinecke can be found in Dalton's New System of Chemical Philosophy, neither is there any suggestion to such an effect unless the somewhat cryptic sentence printed below in italics can have this signification read into it. On the contrary, two of the three lists of atomic weights that were published at different times by Dalton himself, contain one or more atomic weights that are not whole numbers. The third list, in which all are whole numbers, is that of 1808, at p. 219 of Part I of the New System and even this list is not in complete agreement with the text, as regards the atomic weight of carbon, where, on p. 215, carbonic oxide and carbonic acid are mentioned. There Dalton states, as one of four conclusions :—

> That carbonic oxide is a binary compound, consisting of one atom of charcoal, and one of oxygen, together weighing nearly 12 ; that carbonic acid is a ternary compound, (but sometimes binary) consisting of one atom of charcoal, and two of oxygen, weighing 19 ; etc., etc. *In all these cases the weights are expressed in atoms of hydrogen, each of which is denoted by unity.*‡

The atomic weights in the list which accompanies this statement include carbon : 5 and oxygen : 7. What the significance of the word "nearly" before "12" may be is left unexplained, as also why it is not repeated before "19."

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* Journal für Chemie und Physik, **27** (1819), 46.

† See preceding page.

‡ The relative portions of Dalton's New System are reproduced in A. C. Reprint No. 2, pp. 30-33.

Passing next to Part II of the New System, dated 1810, Dalton writes at p. 237:—

> From the various combinations of charcoal with other elements hereafter to be mentioned, the weight of its ultimate particle is deduced to be 5, or perhaps 5·4, that of hydrogen being denoted by unity.

No explanation is given for the "perhaps 5·4" of this quotation nor of where the "5" comes from.

On p. 368, introducing the compounds of "Oxygen with Carbone" we read:—

> The weight of an atom of carbone or charcoal, has not yet been investigated. Of the two compounds, carbonic acid is that which has been longest known, and the proportion of its elements more generally investigated. It consists of nearly 28 parts of charcoal by weight, united to 72 of oxygen. Now as the weight of an atom of oxygen has been determined already to be 7; we shall have the weight of an atom of carbone = 2·7, supposing carbonic acid a binary compound; but 5·4, if we suppose it a ternary compound.

At p. 377 Dalton states:—

> An atom of carbonic oxide consists then of one of carbone or charcoal, weighing 5·4, and one of oxygen, weighing 7, together making 12·4.

And at p. 382:—

> Carbonic acid then appears to be a ternary compound, consisting of one atom of charcoal and two of oxygen; and as their relative weights in the compound are as 28 : 72, we have 36 : 28 : : 7 : 5·4 = the weight of an atom of charcoal; and the weight of an atom of carbonic acid is 19·4 times that of hydrogen.

It seems clear from these quotations from Part II of Dalton's New System that in 1810 he had no idea of the generalisation referred to by Meinecke.

In addition to all this, the assertion contained in the first part of the sentence quoted on p. 11 from Meinecke seems to receive refutation from the concluding clause, inasmuch as this indicates that Dalton's values were arrived at without their being accurately calculated from available analyses and were therefore, at best, mere approximations. Hence it does not appear that the suggestion of Dalton having anticipated Prout can be seriously maintained.

Another contemporary reference to Meinecke may find a place here. In an article entitled "History of Physical Science from the Commencement of the Year 1817, Part I," Thomson reproduced a Table of the Specific Gravities of Gases from the paper by Meinecke in the Annalen der Physik (Gilbert), already referred to, and observed:—

> These specific gravities approach very nearly those which I have adopted in the last edition of my System of Chemistry. Hydrogen, and oxygen, and chlorine, are the very same that had been previously assigned by Dr Prout. I have myself no doubt whatever of their accuracy; and suspect that Meinecke has been influenced by Dr Prout's paper, though he has taken no notice of it. Meinecke adds some further reason for considering the specific gravity of hydrogen as only one sixteenth of that of oxygen. Dr Prout's arguments are sufficiently strong to convince every person who will take the trouble to examine them, and is capable of understanding them. Some additional evidences are given in the paper at present before me.*

In referring to Prout's 1815 paper in his "Introduction to the Atomic Theory" (Oxford, 1831) at pp. 39-40, Daubeny observed with respect to the views expressed there:—

> I believe indeed that I shall not be misrepresenting Dr Prout's opinions, if I remark that, in the paper alluded to, he seems to have noticed the relation between the numbers which, on the authority of other chemists, he gives

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* Annals of Philosophy, **12** (1818), 10.

> as the atomic weights of the several elementary substances enumerated, chiefly as a presumption in favour of the idea of their being possibly compounded of oxygen and hydrogen, of which they appeared to be multiples.
>
> Indeed, if we could ascertain, that there were any two or three undecompounded substances, to whose atomic weight those of all other bodies in nature bore this relation, we might with some degree of plausibility conjecture, that these were the elements out of which the rest were formed; but there is no necessity for assuming, that one of them would prove to be hydrogen, or even any other of the bodies which have yet come under our cognisance.

These observations elicited from Prout the following comments in the course of a letter to Daubeny who had submitted to him the sheets of his "Introduction" prior to publication:—

> In page 39 you observe, "I believe, indeed, that I shall not be misrepresenting Dr Prout's opinions, if I remark that in the paper alluded to he seems to have noticed the relation between the numbers . . . chiefly as a presumption in favour of the idea of their being possibly compounded of oxygen and hydrogen, of which they appear to be multiples." The original opinion to which I was led by the observations of others, and innumerable experiments (never published) of my own, was, that the combining or atomic weights of bodies bear simple relations to one another, frequently by multiple, and consequently that many of them must necessarily be multiples of some one unit; but as the atom of hydrogen, the lowest body known, is frequently subdivided when in combination with oxygen, &c. there seems to be no reason why bodies still lower in the scale than hydrogen (similarly however related to one another, as well as to those above hydrogen) may not exist, of which other bodies may be multiples, without being actually multiples of the intermediate hydrogen. Such was my *opinion* in general terms; my *speculations*, I confess, went further, and were indeed pretty much as you have stated them to be.*

It is of interest to note that Prout in suggesting in this letter to Daubeny the possible existence of substances with atomic weights smaller than that of hydrogen and thus of a possible smaller unit of comparison, anticipated by a considerable number of years any corresponding idea on the part of Marignac and of Dumas.

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* Daubeny's "Introduction," pp. 129-130; also in the Second Edition, Oxford, 1850, p. 471.

The simplicity and plausibility of the hypothesis that the atomic weights of other elements were multiples by whole numbers of that of hydrogen, in course of time attracted much attention and created the incentive to test its validity. This resulted in extended investigations being undertaken by various chemists with a view to verifying the atomic weights both of the elements which were in close or moderately close agreement with the hypothesis and of those—that of chlorine in particular—which showed distinct divergence from it. Besides the determinations already referred to, which were made by Thomson and by Berzelius, further important investigations were carried out, prior to 1860, by Turner, Penny, Dumas and Stas in collaboration, Erdmann and Marchand in collaboration, Marignac, Pelouze, Stas and Dumas independently, and various others. The general result of these investigations was to establish that although, in the cases examined, there was not always close agreement with the hypothesis, the divergences were considerable in comparatively few of them, while in a number of those that had been submitted to the most careful examination the approximation was so close that it was difficult to avoid the conclusion that there must exist some underlying regularity which it was suggested that future investigations might perhaps reveal.

Two specially important papers appeared in 1860. One of these was by Stas in which he described in full detail his elaborate experiments in atomic weight determinations and stated the conclusions with respect to Prout's Hypothesis to which these had led him: the other was by Marignac and was really a commentary upon that of Stas and presented its author's views as opposed to those of Stas. Those portions of the paper by Stas which include his general remarks and conclusions are reproduced in this reprint (pp. 41-47) and the comments of Marignac are given in full (pp. 48-58). The conclusions reached in these papers by Stas and Marignac respectively, faithfully reflect the two aspects of the matter as it presented itself to the minds of contemporary chemists. Between the date of their publication and the earlier years of the twentieth century, notwithstanding the new direction given to thought and the impetus to experimental re-examination resulting from the introduction and elaboration of the Periodic System, the question of the existence of some simple relationship between the atomic weights of other elements and that of hydrogen (or oxygen) merely remained as a subject of frequent remark and discussion, but one about which there appeared to be little prospect of general agreement. Noteworthy statements of contemporary opinion which appeared in addresses or papers by, amongst others, Mallet,* Mendelejeff,† Julius Thomsen,‡ and Strutt,§ showed clearly enough that the problem was unsettled and that data were not yet in sight by the aid of which finality might be reached.

Subsequent to 1895, the progress of physical and physico-chemical investigation shed an entirely new and unexpected light upon the subject. The discovery of X-rays, the study of the cathode rays, the electron theory, the isolation of radium and the investigation of

* Phil. Trans. **171** (1880), 1033.

† Journ. Chem. Soc. **55** (1889), 643.

‡ Copenhagen Oversigt, **1893**, 356; **1894**, 325.

§ Phil. Mag. [6], **1** (1901), 311.

its remarkable properties, including its disintegration, and the observation and investigation of isotopes led to the views now held with respect to the complex character of the Daltonian atoms and to the idea of many elements as consisting of mixtures of isotopes and furnished an explanation for the previously observed discrepancies between the experimental facts concerning atomic weights and the original Prout's Hypothesis.

Obviously there is not room in this introduction for a detailed account of the rehabilitation of Prout's hypothesis as effected by these recent advances. It will be more appropriate, in any case, to examine the matter here mainly from the reverse point of view, in other words to consider how certain features of our modern theory of atomic structure have been anticipated by inspired suggestions based directly upon the hypothesis of Prout.

The most noteworthy instance of this type, perhaps, is the "audacious speculation" put forward by Sir William Crookes in his presidential address to the Chemistry Section of the British Association at Birmingham in 1886.* Crookes discussed here the "first riddle of chemistry"—What are the elements? His manner of approach towards the problem is exhibited in the following extract:

> Just as to Columbus long philosophic meditation led him to the fixed belief of the existence of a yet untrodden world beyond that waste of Atlantic waters, so to our most keen-eyed chemists, physicists, and philosophers a variety of phenomena suggest the conviction that the elements of ordinary assumption are not the ultimate boundary in this direction of the knowledge which man may hope to attain. Well do I remember, soon after I had obtained evidence of the distinct nature of thallium, that Faraday said to me, "To discover a new element is a very fine thing, but if you could decompose an element and tell us what it is

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* Report, British Association, 1886, 558-576.

made of—that would be a discovery indeed worth making." And this was no new speculation of Faraday's, for in one of his early lectures he remarked, "At present we begin to feel impatient, and to wish for a new state of chemical elements. For a time the desire was to add to the metals, now we wish to diminish their number. . . . To decompose the metals, then, to reform them, to change them from one to another, and to realise the once absurd notion of transmutation are the problems now given to the chemist for solution."

After putting the question whether the seventy elements then known might not all have been evolved from some few antecedent forms of matter, or possibly from only one such, for which he subsequently proposed the name *protyle*, Crookes admitted that direct evidence of transmutation of elements was entirely lacking, but proceeded to consider the conclusion first arrived at by Herschel, and pursued later by Clerk-Maxwell, that "atoms bear the impress of manufactured articles." A manufactured article must imply a raw material. What or where was this raw material? This query brought Crookes immediately into contact with Prout's hypothesis, as will be seen from a second extract:—

> And this leads us up to a hypothesis which, if capable of full demonstration, would show us that the accepted elements are not coequal, but have been formed by a process of expansion or evolution. I refer to the well-known hypothesis of Prout, which regards the atomic weights of the elements as multiples, by a series of whole numbers, of unity = the atomic weight of hydrogen. Everyone is aware that the recent more accurate determinations of the atomic weights of different elements do not by any means bring them into close harmony with the values which Prout's law would require. Still in no small number of cases the actual atomic weights approach so closely to those which the hypothesis demands that we can scarcely regard the coincidence as accidental. Accordingly, not a few chemists of admitted eminence consider that we have here an expression of the truth, masked by some residual or collateral phenomena which we have not yet succeeded in eliminating.

> The original calculations on which the most accurate numbers for the atomic weights are founded have recently been recalculated by Mr F. W. Clarke. In his concluding remarks, speaking of Prout's law, Mr Clarke says that "none of the seeming exceptions are inexplicable. In short, admitting half-multiples as legitimate, it is more probable that the few apparent exceptions are due to undetected constant errors than that the great number of close agreements should be merely accidental. I began this recalculation of the atomic weights with a strong prejudice against Prout's hypothesis, but the facts as they came before me have forced me to give it a very respectful consideration."

Crookes's suggestion that the existence of half-multiples might be explained by the assumption that helium, at that time known only spectroscopically, possessed an atomic weight half that of hydrogen, was not—as subsequent events proved—a happy one, but the cosmic speculations in which he next indulged were far more fortunate. Imagining that at the very beginnings of time the original *protyle* alone was existent in an ultra-gaseous state in an inconceivably hot universe, Crookes continued as follows:

> But in course of time some process akin to cooling, probably internal, reduces the temperature of the cosmic *protyle* to a point at which the first step in granulation takes place; matter, as we know it, comes into existence, and atoms are formed. As soon as an atom is formed out of *protyle* it is a store of energy, potential (from its tendency to coalesce with other atoms by gravitation or chemically) and kinetic (from its internal motions). To obtain this energy the neighbouring *protyle* must be refrigerated by it, and thereby the subsequent formation of other atoms will be accelerated. But with atomic matter the various forms of energy which require matter to render them evident begin to act; and, amongst others, that form of energy which has for one of its factors what we now call *atomic weight*. Let us assume that the elementary *protyle* contains within itself the potentiality of every possible combining proportion or atomic weight. Let it be granted that the whole of our known elements were not at this epoch simultaneously created. The easiest formed

element, the one most nearly allied to the *protyle* in simplicity, is first born. Hydrogen—or shall we say helium?—of all the known elements the one of simplest structure and lowest atomic weight, is the first to come into being.

The almost uncanny anticipation of the transmutability of energy and matter contained in the foregoing paragraph has not attracted the attention which it deserves. The succeeding item in the argument, however, the prophecy of isotopes, is more familiar through its frequent quotation in modern monographs on atomic structure.

I have said that the original *protyle* contained within itself the potentiality of all possible atomic weights. It may well be questioned whether there is an absolute uniformity in the mass of every ultimate atom of the same chemical element. Probably our atomic weights merely represent a mean value around which the actual atomic weights of the atoms vary within certain narrow limits.

Each well-defined element represents a platform of stability connected by ladders of unstable bodies. In the first accreting together of the primitive stuff the smallest atoms would form, then these would join together to form larger groups, the gulf across from one stage to another would be gradually bridged over, and the stable element appropriate to that stage would absorb, as it were, the unstable rungs of the ladder which led up to it. I conceive, therefore, that when we say the atomic weight of, for instance, calcium is 40, we really express the fact that, while the majority of calcium atoms have an actual atomic weight of 40, there are not a few which are represented by 39 or 41, a less number by 38 or 42, and so on. We are here reminded of Newton's "old worn particles."

Is it not possible, or even feasible, that these heavier and lighter atoms may have been in some cases subsequently sorted out by a process resembling chemical fractionation? This sorting out may have taken place in part while atomic matter was condensing from the primal state of intense ignition, but also it may have been partly effected in geological ages by successive solutions and reprecipitations of the various earths.

This may seem an audacious speculation, but I do not think it is beyond the power of chemistry to test its feasibility.

The experimental work of Crookes on the rare earth metals, where he assumed excessive and systematic fractionation to act the part of a chemical "sorting Demon," distributing the atoms of a single element into meta-elements * with different atomic weights, proved fallacious, and it was not until 1910 that the possibility that atoms might differ in weight while possessing exactly the same chemical properties suggested itself anew to Professor Soddy, † in connection with his work on radioactivity. Shortly afterwards, the technique of Sir J. J. Thomson's method of positive ray analysis ‡ was so improved by F. W. Aston § as to permit its use for the distinction of the duality of neon (atomic weight, 20·2; isotopic masses, 20 and 22), and it is interesting to note that the definite announcement of both Soddy's and Aston's conclusions regarding isotopes was made in two simultaneous papers presented to the British Association at Birmingham in 1913, ‖ twenty-seven years after Crookes had uttered his prophetic address in the same city.

The approaching centenary of Prout's hypothesis was also celebrated in 1913 by the publication of Moseley's classical article on atomic numbers, ¶ which afforded final justification to the theory of the nuclear atom formulated in 1911 by Sir Ernest Rutherford **—itself a logical amplification of Thomson's earlier electronic models. The root idea that all atoms consisted of aggregates of *protons* * and *electrons* gained immediate and universal acceptance, and with Aston's mass-spectrographic data indicating that the true atomic masses of all isotopic elements were essentially whole numbers, Prout's hypothesis appeared to achieve complete vindication. The only weak link in the whole chain of evidence lay in the fact that the first element, hydrogen, instead of providing the anticipated unitary basis for the whole series, constituted an undoubted exception with an atomic weight of 1·0078.

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* Journ. Chem. Soc. **53** (1888), 487-504.

† Chem. Soc. Annual Report, 1910, 285.

‡ "Rays of Positive Electricity and their Application to Chemical Analysis": Longmans, 1913.

§ "Isotopes": Arnold, 1922.

‖ Report, British Association, 1913, 403 and 445.

¶ Phil. Mag. [6] **26**, (1913), 1031.

** *Ibid.* [6] **21**, (1911), 669.

To explain this abnormality of hydrogen, there has been advanced the assumption of a "packing effect," which may be stated in Aston's own words †:—

> In the nuclei of normal atoms the packing of the electrons and protons is so close that the additive law of mass will not hold and the mass of the nucleus will be less than the sum of the masses of its constituent charges.

Perhaps the most remarkable point in the whole history of Prout's hypothesis is the anticipation of this packing effect by Marignac ‡ as long ago as 1860. Convinced, in spite of the experimental results of Stas, that the fundamental principle which induced Prout to formulate his hypothesis—the idea of the unity of matter—was valid, Marignac argued as follows:

> Could we not suppose that the cause (unknown but probably different from the physical and chemical agencies familiar to us) which has determined certain groupings of the atoms of the sole primordial matter so as to give rise to our chemical atoms, by impressing on each of these groups a special character and particular properties, should not at the same time have exercised an influence on the manner according to which these groups of primordial atoms would obey the law of universal attraction, in such

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* The name *proton* for the "atom" of positive electricity was suggested at the Cardiff meeting of the British Association in 1920.

† "Isotopes": p. 101.

‡ See p. 58 of this reprint.

wise that the weight of each group might not be exactly the sum of the weights of the primordial atoms composing it?

No means of following up a supposition of this kind was available until Einstein's theory of relativity was developed, so that it is not to be wondered at that Marignac's suggestion was entirely disregarded by his contemporaries.

Just as improvements in analytical technique in the first half of the last century demonstrated that atomic weights were not exactly integral, so during the last few years more accurate mass-spectrographic measurements by Aston have forced the abandonment of the whole-number rule for isotopic masses. The packing effect is not constant; it varies in a regular way as the complexity of the nucleus is increased.* But although this has necessitated once more a departure from the integral simplicity of Prout's hypothesis, as re-stated in the language of modern physics, the really important basic idea of Prout—the common constitution of all elements—now stands unquestioned. The only change in our point of view is that two components—protons and electrons—replace the original "Urstoff" or "protyle," and recent discussions held by the Royal Society on the structure of atomic nuclei † show that a complete knowledge of the actual arrangement of these within the nucleus itself cannot long be delayed.

A final point of interest may be very briefly mentioned. Fierce controversy has been waged in the past regarding the rival claims of H = 1 and of O = 16 as a basis for atomic weights, and Prout's hypothesis has frequently been adduced as an argument in support of the former choice. While the recognition of the packing effect has amply justified the final selection by chemists of the basis O = 16, it may be noted here that the discovery that oxygen is not absolutely homogeneous, but contains traces of isotopes with masses 17 and 18,* involves the fact that the true mass of the main isotope is not exactly 16 on our present basis, and although the divergence is so slight that it may for the moment be disregarded by the chemist, the physicist † already finds himself compelled to take it into account. Hydrogen also, it appears, is similarly complex, containing a small quantity of an isotope with mass 2.‡ This does not exist in nearly sufficient quantity to reduce the true mass of the lighter hydrogen isotope from 1·0078 to unity, but a slight downward revision will certainly be necessary.

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* See Proc. Roy. Soc. **123** A, (1929), 380.

† Proc. Roy. Soc. **123** A (1929), 373; **136** A (1932), 735.

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* Giauque and Johnston: Journ. Amer. Chem. Soc. **51** (1929), 1436 and 3528.

† See Aston: Nature, **126** (1930), 953.

‡ Urey, Brickwedde, and Murphy, Physical Review, **39** (1932), 164.

ON THE RELATION BETWEEN THE SPECIFIC GRAVITIES OF BODIES IN THEIR GASEOUS STATE AND THE WEIGHTS OF THEIR ATOMS.*

[By William Prout.]

The author of the following essay submits it to the public with the greatest diffidence; for though he has taken the utmost pains to arrive at the truth, yet he has not that confidence in his abilities as an experimentalist as to induce him to dictate to others far superior to himself in chemical acquirements and fame. He trusts, however, that its importance will be seen, and that some one will undertake to examine it, and thus verify or refute its conclusions. If these should be proved erroneous, still new facts may be brought to light, or old ones better established, by the investigation; but if they should be verified, a new and interesting light will be thrown upon the whole science of chemistry.

It will perhaps be necessary to premise that the observations about to be offered are chiefly founded on the doctrine of volumes as first generalized by M. Gay-Lussac; and which, as far as the author is aware at least, is now universally admitted by chemists.

On the Specific Gravities of the Elementary Gases.

1. *Oxygen and Azote.*—Chemists do not appear to have considered atmospheric air in the light of a compound formed upon chemical principles, or at least

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[* From *Annals of Philosophy*, 6 (1815), 321-330.]

little stress has been laid upon this circumstance. It has, however, been long known to be constituted by bulk of four volumes of azote and one volume of oxygen; and if we consider the atom of oxygen as 10, and the atom of azote as 17·5, it will be found by weight to consist of one atom of oxygen and two atoms of azote, or per cent. of

Oxygen	22·22
Azote	77·77

Hence, then, it must be considered in the light of a pure chemical compound; and indeed nothing but this supposition will account for its uniformity all over the world, as demonstrated by numerous experiments. From these data the specific gravities of oxygen and azote (atmospheric air being 1·000) will be found to be,*

Oxygen	1·1111
Azote	·9722

2. *Hydrogen.*—The specific gravity of hydrogen, on account of its great levity, and the obstinacy with which it retains water, has always been considered as the most difficult to take of any other gas. These obstacles made me (to speak in the first person) despair of arriving at a more just conclusion than had been before obtained by the usual process of weighing; and it occurred to me that its specific gravity might be much more accurately obtained by calculation from the specific

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* Let x = sp. gr. of oxygen. 22·22 = a
y = sp. gr. of azote. 77·77 = b
Then $\frac{x+4y}{5}=1$.
And $x : 4y :: a : b$.
Hence $5-4y=\frac{4ay}{b}$.
And $y=\frac{5b}{4a+4b}=\cdot9722$. And $x=5-4y=1\cdot11111$

gravity of a denser compound into which it entered in a known proportion. Ammoniacal gas appeared to be the best suited to my purpose, as its specific gravity had been taken with great care by Sir H. Davy, and the chance of error had been much diminished from the slight difference between its sp. gr. and that of steam. Moreover, Biot and Arrago had obtained almost precisely the same result as Sir H. Davy. The sp. gr. of ammonia, according to Sir H. Davy, is ·590164, atmospheric air being 1·000. We shall consider it as ·5902; and this we are authorized in doing, as Biot and Arrago state it somewhat higher than Sir H. Davy. Now ammonia consists of three volumes of hydrogen and one volume of azote condensed into two volumes. Hence the sp. gr. of hydrogen will be found to be ·0694,* atmospheric air being 1·0000. It will be also observed that the sp. gr. of oxygen as obtained above is just 16 times that of hydrogen as now ascertained, and the sp. gr. of azote just 14 times.†

3. *Chlorine.*—The specific gravity of muriatic acid, according to Sir H. Davy's experiments, which coincide exactly with those of Biot and Arrago, is 1·278. Now if we suppose this sp. gr. to be erroneous in the same proportion that we found the sp. gr. of oxygen and azote to be above, (which, though not rigidly accurate, may yet be fairly done, since the experiments were conducted in a similar manner), the sp. gr. of this gas will come out about 1·2845;‡ and since it is a

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* Let x = sp. gr. of hydrogen.

$$\text{Then } \frac{3x + \cdot 9722}{2} = \cdot 5902.$$

$$\text{Hence } x = \frac{1\cdot 1804 - \cdot 9722}{3} = \cdot 0694.$$

† 1·11111 ÷ ·0694 = 16. And ·9722 ÷ ·0694 = 14.

‡ As 1·104 : 1·11111 :: 1·278 : 1·286.
And as ·969 : ·9722 :: 1·278 ; 1·283. The mean of these is 1·2845.

compound of one volume chlorine and one volume hydrogen, the specific gravity of chlorine will be found by calculation to be 2·5.* Dr Thomson states, that he has found 2·483 to be near the truth,† and Gay-Lussac almost coincides with him.‡ Hence there is every reason for concluding that the sp. gr. of chlorine does not differ much from 2·5. On this supposition, the sp. gr. of chlorine will be found exactly 36 times that of hydrogen.

On the Specific Gravities of Elementary Substances in a Gaseous State that do not at ordinary Temperatures exist in that State.

1. *Iodine.* — I had some reason to suspect that M. Gay-Lussac had in his excellent memoir rated the weight of an atom of this substance somewhat too high; and in order to prove this 50 grains of iodine, which had been distilled from lime, were digested with 30 grs. of very pure lamellated zinc. The solution formed was transparent and colourless; and it was found that 12·9 grains of zinc had been dissolved. 100 parts of iodine, therefore, according to this experiment, will combine with 25·8 parts of zinc, and the weight of an atom of iodine will be 155,§ zinc being supposed to be 40. From these data, the sp. gr. of iodine in a state of gas

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* Let $x =$ sp. gr. of chlorine.

$$\text{Then } \frac{x + \cdot 0694}{2} = 1 \cdot 2845.$$

And $x = 2 \cdot 569 - \cdot 0694 = 2 \cdot 5$ very nearly.

† *Annals of Philosophy*, vol. iv. p. 13.

‡ Ditto, vol. vi. p. 126.

§ As 25·8 : 100 :: 40 : 155. According to experiment 8th, stated below, the weight of an atom of zinc is 40. Dr Thomson makes it 40·9, which differs very little. See *Annals of Philosophy*, vol. iv. p. 94.

will be found by calculation to be 8·61111, or exactly 124 times that of hydrogen.*

2. *Carbon.*—I assume the weight of an atom of carbon at 7·5. Hence the sp. gr. of a volume of it in a state of gas will be found by calculation to be ·4166, or exactly 12 times that of hydrogen.

3. *Sulphur.*—The weight of an atom of sulphur is 20. Hence the specific gravity of its gas is the same as that of oxygen, or 1·1111, and consequently just 16 times that of hydrogen.

4. *Phosphorus.*—I have made many experiments in order to ascertain the weight of an atom of this substance; but, after all, have not been able to satisfy myself, and want of leisure will not permit me to pursue the subject further at present. The results I have obtained approached nearly to those given by Dr Wollaston, which I am therefore satisfied are correct, or nearly so, and which fix phosphorus at about 17·5, and phosphoric acid at 37·5,† and these numbers at present I adopt.

5. *Calcium.*—Dr Marcet found carbonate of lime composed of 43·9 carbonic acid and 56·1 lime.‡ Hence

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* One volume of hydrogen combines with only half a volume of oxygen, but with a whole volume of gaseous iodine, according to M. Gay-Lussac. The ratio in volume, therefore, between oxygen and iodine is as ½ to 1, and the ratio in weight is as 1 to 15·5. Now ·5555, the density of half a volume of oxygen, multiplied by 15·5, gives 8·61111, and 8·61111 ÷ ·06944 = 124. Or generally, to find the sp. gr. of any substance in a state of gas, we have only to multiply half the sp. gr. of oxygen by the weight of the atom of the substances with respect to oxygen. See *Annals of Philosophy*, vol. v. p. 105.

† Some of my experiments approached nearer to 20 phosphorus and 40 phosphoric acid.

‡ I quote on the authority of Dr Thomson, *Annals of Philosophy*, vol. iii. p. 376. Dr Wollaston makes it somewhat different, or that carbonate of lime consists of 43·7 acid and 56·3 lime. Phil. Trans. vol. civ. p. 8.

as 43·9 : 56·1 :: 27·5 : 35·1, or 35 very nearly; and 35 − 10 = 25, for the atom of calcium. The sp. gr. of a volume of its gas will therefore be 1·3888, or exactly 20 times that of hydrogen.

6. *Sodium.*—100 grains of dilute muriatic acid dissolved 18·6 grs. of carbonate of lime, and the same quantity of the same dilute acid dissolved only 8·2 grs. of carbonate of lime, after there had been previously added 30 grs. of a very pure crystallized subcarbonate of soda. Hence 30 grs. of crystallized subcarbonate of soda are equivalent to 10·4 grs. of carbonate of lime, and as 10·4 : 30 :: 62·5 : 180. Now 100 grs. of crystallized subcarbonate of soda were found by application of heat to lose 62·5 of water. Hence 180 grs. of the same salt contain 112·5 water, equal to 10 atoms, and 67·5 dry subcarbonate of soda, and 67·5 − 27·5 = 40 for the atom of soda, and 40 − 10 = 30 for the atom of sodium. Hence a volume of it in a gaseous state will weigh 1·6666, or exactly 24 times that of hydrogen.

7. *Iron.*—100 grs. of dilute muriatic acid dissolved as before 18·6 grs. of carbonate of lime, and the same quantity of the same acid dissolved 10·45 of iron. Hence as 18·6 : 10·45 :: 62·5 : 35·1, or for the sake of analogy, 35, the weight of an atom of iron. The sp. gr. of a volume of this metal in a gaseous state will be 1·9444, or exactly 28 times that of hydrogen.

8. *Zinc.*—100 grs. of the same dilute acid dissolved; as before, 18·6 of carbonate of lime and 11·85 of zinc. Hence as 18·6 : 11·85 :: 62·5 : 39·82, the weight of the atom of zinc, considered from analogy to be 40. Hence the sp. gr. of a volume of it in a gaseous state will be 2·222, or exactly 32 times that of hydrogen.

9. *Potassium.*—100 grs. of the same dilute acid dissolved, as before, 18·6 carbonate of lime; but after the addition of 20 grs. of super-carbonate of potash,

only 8·7 carbonate of lime. Hence 20 grs. of super-carbonate of potash are equivalent to 9·9 carbonate of lime; and as 9·9 : 20 :: 62·5 : 126·26, the weight of the atom of super-carbonate of potash. Now 126·26 − 55 + 11·25 = 60, the weight of the atom of potash, and 60 − 10 = 50, the weight of the atom of potassium. Hence a volume of it in a state of gas will weigh 2·7777, or exactly 40 times as much as hydrogen.

10. *Barytium.*—100 grs. of the same dilute acid dissolved exactly as much again of carbonate of barytes as of carbonate of lime. Hence the weight of the atom of carbonate of barytes is 125; and 125 − 27·5 = 97·5, the weight of the atom of barytes, and 97·5 − 10 = 87·5, the weight of the atom of barytium. The sp. gr. therefore, of a volume of its gas will be 4·8611, or exactly 70 times that of hydrogen.

With respect to the above experiments, I may add, that they were made with the greatest possible attention to accuracy, and most of them were many times repeated with almost precisely the same results.

The following tables exhibit a general view of the above results, and at the same time the proportions, both in volume and weight, in which they unite with oxygen and hydrogen: also the weights of other substances, which have not been rigidly examined, are here stated from analogy.

TABLE I.—*Elementary Substances.*

Name.	Sp. gr. hydr being 1.	Wt. of atom, 2 vols. hydr. being 1.	Wt. of atom, oxygen being 10.	Wt. of atom, oxygen being 10, from experiment.	Sp. gr. atmospheric air being 1.	Sp. gr. atmospheric air being 1, from experiment.	Wt. in grs. of 100 cub. inches. Barom. 30, Therm. 60.	Wt. in grs. of 100 cub. in. from exper.	Observations.
Hydrogen ..	1	1	1·25	1·32	·06944	·073 [1]	2·118	2·23	[1] Dr. Thomson. See *Annals of Philosophy*, i. 177.
Carbon	6	6	7·5	7·54 [2]	·4166	—	12·708	—	[2] Dr. Wollaston, from Biot and Arrago. Phil. Trans. civ. 20. Dr. Thomson makes it 7·51. *Annals of Philosophy*, ii. 42.
Azote	14	14	17·5	17·54	·9722	·969 [3]	29·652	29·56	[3] Dr. W. from Biot and Arrago.
Phosphorus..	14	14	17·5	17·4 [4]	·9722	—	29·652	—	[4] Dr. W. from Berzelius and Rose.
Oxygen......	16	8	10	10	1·1111	1·104 [5]	33·888	33·672	[5] Dr. Thomson, from a mean of several experiments.
Sulphur......	16	16	20	20 [6]	1·1111	—	33·888	—	[6] Dr. W. from Berzelius.
Calcium	20	20	25	25·46 [7]	1·3888	—	42·36	—	[7] Dr. W. from experiment.
Sodium	24	24	30	29·1 [8]	1·6666	—	50·832	—	[8] Dr. W. from Davy.
Iron	28	28	35	34·5 [9]	1·9444	—	59·302	—	[9] Dr. W. from Thenard and Berzelius.
Zinc	32	32	40	41 [10]	2·222	—	67·777	—	[10] Dr. W. from Gay-Lussac.
Chlorine	36	36	45	44·1 [11]	2·5	2·483 [12]	76·248	—	[11] Dr. W. from Berzelius. [12] Quoted from Dr. Thomson, *Annals of Philosophy*, iv. 13.
Potassium ...	40	40	50	49·1 [13]	2·7777	—	84·72	—	[13] Dr. W. from Berzelius.
Barytium ...	70	70	87·5	87 [14]	4·8611	—	148·26	—	[14] Dr. W. from Berzelius and Klaproth.
Iodine	124	124	155	156·21 [15]	8·6111	—	262·632	—	[15] Gay-Lussac. Ann. de Chim. xci. 5.

TABLE II.—*Combinations with Oxygen.*

Name.	Sp. gr. hydro. being 1.	Wt. of atom, 2 vol. hydro. being 1.	Wt. of atom, ox. being 10.	Wt. of atom, ox. being 10, from exper.	Sp. gr. atmos. air being 1.	Sp. gr. atmos. air being 1, from exper.	Wt. of 100 cu. in. Bar. 30, Ther. 60.	Wt. of 100 cu. in. from exp.	Elements by volume.	No. of vol. after combination.	Elements by weight.	Observations.
Water	9	9	11·25	11·32	·625	·6896 [1]	19·062	21·033	·5 ox + 1 hyd	1	1 ox + 1 hy	[1] Trales, Dr. Thomson, *Annals*, i. 177.
Carbonic oxyde ..	14	14	17·5	17·54	·9722	·956 [2]	29·652	29·16	·5 ox + 1 ca	1	1 ox + 1 car	[2] Cruikshanks, quoted by Thomson.
Nitrous oxyde....	22	22	27·5	—	1·5277	1·614 [3]	46·596	49·227	·5 ox + 1 az	1	1 ox + 1 az	[3] Sir H. Davy.
Atmospheric air..	14·4	36	45	—	1·000	1·000	30·5	30·5 [4]	·5 ox + 2 az	2·5	1 ox + 2 az	[4] Sir G. S. Evelyn.
Phosphorous acid									·5 ox + 1 ph ?		1 ox + 1 ph ?	
Oxyde of sulphur?									·5 ox + 1 sul ?		1 ox + 1 sul ?	
Euchlorine	44	44	55		3·0555	2·409 [5]	93·192	73·474	·5 ox + 1 ch	1 ?	1 ox + 1 ch	[5] Sir H. Davy.
									·5 ox + 1 iod		1 ox + 1 iod	
Lime	28	28	35	35·46	1·9444	—	59·304	—	·5 ox + 1 cal		1 ox + 1 cal	
									&c.		&c.	
									1 ox + 1 hy [6]		2 ox + 1 hy	[6] This and all higher combinations of
Carbonic acid ..	22	22	27·5	27·54	1·5277	1·518 [7]	46·596	46·313	1 ox + 1 car	1	2 ox + 1 car	hydrogen with oxygen are unknown.
Nitrous gas	15	30	37·5		1·0416	1·0388 [8]	31·77	31·684	1 ox + 1 az	2	2 ox + 1 az	[7] Saussure.
Phosphoric acid..	30	30	37·5	37·4	2·0832	—	63·54	—	1 ox + 1 ph		2 ox + 1 ph	[8] Berard.
Sulphurous acid ..	32	32	40		2·2222	2·193 [9]	67·777	66·89	1 ox + 1 sul	1	2 ox + 1 sul	[9] Sir H. Davy.
									1 ox + 1 ch		2 ox + 1 ch	
									1 ox + 1 iod		2 ox + 1 iod	
									&c.		&c.	
									1·5 ox + 1 car		3 ox + 1 car	
Nitrous acid	38	38	47·5		2·6388	2·427 [10]	80·484	74·0234	1·5 ox + 1 az	1	3 ox + 1 az	[10] Sir H. Davy.
									1·5 ox + 1 ph		3 ox + 1 ph	
Sulphuric acid....	40	40	50	50	2·7777		84·72		1·5 ox + 1 sul	1	3 ox + 1 sul	
									1·5 ox + 1 ch		3 ox + 1 ch	
									1·5 ox + 1 iod		3 ox + 1 iod	
									&c.		&c.	
									2·5 ox + 1 car		5 ox + 1 car	
Nitric acid	54	54	67·5	67·54	3·75		114·372		2·5 ox + 1 az	1	5 ox + 1 az	
									2·5 ox + 1 ph		5 ox + 1 ph	See Gay-Lussac's memoir on iodine
									2·5 ox + 1 sul		5 ox + 1 sul	above referred to.
Chloric acid	76	76	95		5·2777	—	160·968		2·5 ox + 1 ch	1	5 ox + 1 ch	
Iodic acid.	164	164	205		11·3883		347·352		2·5 ox + 1 iod	1	5 ox + 1 iod	
									&c.		&c.	

TABLE III.—*Compounds with Hydrogen.*

Name.	Sp. gr. hydro. being 1.	Wt. of atom, 2 vol. hydr. being 1.	Wt. of atom, oxygen being 10.	Wt. of atom, oxygen being 10, from experiment.	Sp. gr. atmospheric air being 1.	Sp. gr. atmospheric air being 1, from experiment.	Wt. of 100 cub. inch. Bar. 30. Ther. 60.	Wt. of 100 cub. inch. from exper.	Elements by volume.	No. of vol. after combination.	Elements by weight.	Observations.
Carbureted hydrogen....	8	7	8·75	8·86	·5555	·5555 [1]	16·999	16·999	2 hy + 1 car	1	1 hy + 1 car	[1] Dr. Thomson.
Olefiant gas	14	13	16·25	16·4	·9722	·974 [2]	29·652	29·72	2 hy + 2 car	1	1 hy + 2 car	[2] Ditto.
Hydro-phosphorus gas .. Phosphoreted hydrogen..												I have omitted these from the uncertainty that still hangs over phosphoros.
									1 hy + 1 az		·5 hy + 1 az	This compound is at present unknown, but it probably exists in fulminating gold, silver, &c. united to these metals.
Ammonia	8·5	15·5	19·375	21·5 [3]	·5902	·59 [3]	18·003	18·00	3 hy + 1 az	2	1·5 hy + 1 az	[3] Dr. Wollaston.
Sulphureted hydrogen. ..	17	16·5	20·625	20·66	1·1805	1·177 [4]	36·006	35·89	1 hy + 1 sul	1	·5 hy + 1 sul	[4] Sir H. Davy.
Muriatic acid	18·5	36·5	45·625	45·66	1·284	1·278 [5]	39·183	38·979	1 hy + 1 ch	2	·5 hy + 1 ch	[5] Ditto.
Hydriodic acid	62·5	124·5	155·625	155·66	4·3402	4·3463 [6]	132·375		1 hy + 1 iode	2	·5 hy + 1 iod	[6] Gay-Lussac.

TABLE IV.—*Substances stated from Analogy, but of which we are yet uncertain.*

Name.	Sp. gr. hydr. being 1.	Wt. of atom, 2 vol. hydr. being 1.	Wt. of atom, oxygen being 10.	Wt. of atom, ox. being 10, from exper.	Observations.
Aluminum	8	8	10	10·68[1]	[1] Berzelius.
Magnesium	12	12	15	14·6[2]	[2] Henry. Berzelius makes it 15·77
Chromium	18	18	22·5	23·6[3]	[3] Berzelius.
Nickel	28	28	35	36·5[4]	[4] Ditto.
Cobalt	28	28	35	36·6[5]	[5] Rolhoff.
Tellurium......	32	32	40	40·27[6]	[6] Berzelius.
Copper........	32	32	40	40[7]	[7] As deduced by Dr. Thomson.
Strontium......	48	48	60	59[8]	[8] Klaproth.
Arsenic........	48	48	60	60[9]	[9] Berzelius.
Molybdenum ..	48	48	60	60·13[10]	[10] Bucholz and Berzelius.
Manganese	56	56	70	71·15[11]	[11] Berzelius.
Tin............	60	60	75	73·5[12]	[12] Ditto.
Bismuth	72	72	90	89·94[13]	[13] Ditto.
Antimony......	88	88	110	111·11[14]	[14] Ditto. Dr. Thomson makes it 112·49.
Cerium	92	92	115	114·87[15]	[15] Hisinger.
Uranium	96	96	120	120[16]	[16] Bucholz.
Tungsten	96	96	120	121·21[17]	[17] Berzelius.
Platinum	96	96	120	121 66[18]	[18] Ditto.
Mercury	100	100	125	125[19]	[19] Fourcroy and Thenard.
Lead	104	104	130	129·5[20]	[20] Berzelius.
Silver..........	108	108	135	135[21]	[21] Wenzel and Davy.
Rhodium	120	120	150	149·03[22]	[22] Berzelius.
Titanium	144	144	180	180·1[23]	[23] Ditto.
Gold	200	200	250	249·68[24]	[24] Ditto.

Observations.

Table I.—This, as well as the other tables, will be easily understood. In the first column we have the specific gravities of the different substances in a gaseous state, hydrogen being 1 : and if we suppose the volume to be 47·21435 cubic inches, the numbers will at the same time represent the number of grains which this quantity of each gas will weigh. In the third column are the corrected numbers, the atom of oxygen being supposed, according to Dr Thomson, Dr Wollaston,

&c. to be 10: and in the fourth, the same, as obtained by experiment, are stated, to show how nearly they coincide. Of the individual substances mentioned, I have no remark to make, except with respect to iodine. I made but one experiment to ascertain the weight of the atom of this substance, and therefore the results stated may be justly considered as deserving but little confidence; and indeed this would be the case, did not all the experiments of Gay-Lussac nearly coincide in the same.

Table II.—This table exhibits many striking instances of the near coincidence of theory and experiment. It will be seen that Gay-Lussac's views are adopted, or rather indeed anticipated, as a good deal of this table was drawn up before I had an opportunity of seeing the latter part of that chemist's memoir on iodine. That table also exhibits one or two striking examples of the errors that have arisen from not clearly understanding the relation between the doctrine of volumes and of atoms. Thus ammonia has been stated to be composed of one atom of azote and three of hydrogen, whereas it is evidently composed of one atom of azote and only 1·5 of hydrogen, which are condensed into two volumes, equal therefore to one atom; and this is the reason why this substance, like some others, apparently combine in double proportions.*

Table III.—This table likewise exhibits some striking examples of the coincidence above noticed. Indeed, I had often observed the near approach to round numbers of many of the weights of the atoms, before I was led to investigate the subject. Dr Thomson appears also to have made the same remark. It is also worthy of observation, that the three magnetic metals, as noticed

by Dr Thomson, have the same weight, which is exactly double that of azote. Substances in general of the same weight appear to combine readily, and somewhat resemble one another in their nature.

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* See Gay-Lussac's memoir on iodine, *Annals of Philosophy*, vi. 189.

On a general review of the tables, we may notice,

1. That all the elementary numbers, hydrogen being considered as 1, are divisible by 4, except carbon, azote, and barytium, and these are divisible by 2, appearing therefore to indicate that they are modified by a higher number than that of unity or hydrogen. Is the other number 16, or oxygen? And are all substances compounded of these two elements?

2. That oxygen does not appear to enter into a compound in the ratio of two volumes or four atoms.

3. That all the gases, after having been dried as much as possible, still contain water, the quantity of which, supposing the present views are correct, may be ascertained with the greatest accuracy.

Others might doubtless be mentioned; but I submit the matter for the present to the consideration of the chemical world.

⁂ The author of the paper on the "Relation between the Specific Gravity of Gaseous Bodies and the Weight of their Atoms" thinks it proper to state, that many of the numbers in the fourth table in that paper, which are stated to be given on the authority of Berzelius, will be found to differ from those given by that chemist in the *Annals*, v. iii. p. 362, on account of their having been founded on the deductions of others, (principally of Dr. Thomson) from the experiments of Berzelius, and not upon that chemist's own deductions.*

* [This note is printed on p. 472 of the same volume as the original paper.]

CORRECTION OF A MISTAKE IN THE ESSAY ON THE RELATION BETWEEN THE SPECIFIC GRAVITIES OF BODIES IN THEIR GASEOUS STATE AND THE WEIGHTS OF THEIR ATOMS.*

[By WILLIAM PROUT.]

The author of the essay On the Relation between the Specific Gravities of Bodies in their Gaseous State and the Weights of their Atoms is anxious to correct an oversight which influences some of the numbers in the third table given in that essay (vol. vi. p. 328). This oversight will be found in the head or title of the third column in each table, and consists in the statement of the atom of hydrogen being composed of two volumes instead of one, upon which latter supposition the tables are actually constructed, except in the instances corrected in the third table as follows, and in a sentence in the first paragraph on p. 330, beginning "This table also exhibits," &c. which is to be expunged.

In this table it will be also observed that the new determinations of Gay-Lussac respecting the prussic acid, &c. are inserted, to show that they correspond with, and further corroborate, the views which have been brought forward in the essay above referred to.

There is an advantage in considering the volume of hydrogen equal to the atom, as in this case the specific gravities of most, or perhaps all, elementary substances (hydrogen being 1) will either exactly coincide with, or be some multiple of, the weights of their atoms; whereas

[* From *Annals of Philosophy*, **7** (1816), 111-113.]

Name.	Sp. gr. hydro. being 1.	Wt. of atom, hydrogen being 1.	Wt. of atom, oxygen being 10.	Wt. of atom, oxygen being 10, from experiment.	Sp. gr. atmospheric air being 1.	Sp. gr. atmospheric air being 1, from experiment.	Wt. of 100 cub. inch. Bar. 30. Ther. 60.	Wt. of 100 cub. inch. from exper.	Elements by volume.	No. of vol. after condensation.	Elements by weight.	Observations.
Carbureted hydrogen..	8	4	5	5·09	·5555	·5555[1]	16·999	16·999	1 hyd + ·5car	·5	1 hyd + ·5car	[1] Dr. Thomson.
Olefiant gas	14	7	8·75	8·86	·9722	·9740[1]	29·652	29·72	1 hyd + 1 car	·5	1 hyd + 1 car	
Sulphureted hydrogen.	17	17	21·25	21·32	1·1805	1·177	36·006	35·89	1 hyd + 1 sul	1	1 hyd + 1 sul	
Muriatic acid	18·5	37	46·25	45·42	1·284	1·278	39·183	38·979	1 hyd + 1 chl	2	1 hyd + 1 chl	
Hydriodic acid	62·5	125	156·25	157·58	4·3402	4·3463[2]	132·375	—	1 hyd + 1 iod	2	1 hyd + 1 iod	[2] Gay-Lussac.
Ammonia	8·5	17	21·25	21·5[3]	·5902[4]	·5900	18·003	18·000	3 hyd + 1 az	2	3 hyd + 1 az.	[3] Dr. Wollaston. [4] Sir H. Davy.
Cyanogen	26	26	32·5	32·52	1·8055	1·8064[5]	55·068	—	2 car + 1 az	1	2 car + 1 az	[5] Gay-Lussac. Ann. de Chim. Aug. 1815.
Hydro-cyanic acid....	13·5	27	33·75	33·846	·9374	·9360[5]	28·593	—	1 cya + 1 hy	2	1 cya + 1 az	
Chloro-cyanic acid ...	31	62	77·5	—	2·1527	2·1111[5]	65·659	—	1 cya + 1 chl	2	1 cya + 1 chl	

if we make the volume of oxygen unity, the weights of the atoms of most elementary substances, except oxygen, will be double that of their specific gravities with respect to hydrogen. The assumption of the volume of hydrogen being equal to the atom will also enable us to find more readily the specific gravities of bodies in their gaseous state (either with respect to hydrogen or atmospheric air), by means of Dr Wollaston's logometric scale.

If the views we have ventured to advance be correct, we may almost consider the πρώτη ὕλη of the ancients to be realised in hydrogen; an opinion, by the by, not altogether new. If we actually consider this to be the case, and further consider the specific gravities of bodies in their gaseous state to represent the number of volumes condensed into one; or, in other words, the number of the absolute weight of a single volume of the first matter (πρώτη ὕλη) which they contain, which is extremely probable, multiples in weight must always indicate multiples in volume, and *vice versâ;* and the specific gravities, or absolute weights of all bodies in a gaseous state, must be multiples of the specific gravity or absolute weight of the first matter (πρώτη ὕλη), because all bodies in a gaseous state which unite with one another unite with reference to their volume.

EXTRACTS FROM

RESEARCHES ON THE MUTUAL RELATIONS OF ATOMIC WEIGHTS.*

By J. S. STAS, Member of the Academy.

ALL the analytical investigations undertaken for nearly a century lead us to assume that compound substances possess a definite, constant, invariable, composition. To the ratios deduced from these researches the names of *proportional numbers*, of *chemical proportions*, of *chemical equivalents*, of *atoms* have been given in turn. The illustrious Berzelius devoted a great part of his life to fixing the *weights* of the chemical proportions. His investigations on this subject will remain an imperishable monument to his sagacity and genius. The minute and repeated checks to which I have had the assurance or temerity to submit them, have convinced me that his analytical skill has never been surpassed, if indeed it has ever been equalled. Berzelius, we know, concluded from his researches that there is no simple relation between the weights of the atoms of substances; he remained all his life convinced of this truth.

As early as 1815, Dr William Prout, in a memoir entitled "*On the relation between the specific gravities of bodies in their gaseous state and the weights of their atoms*" propounded the idea that the atomic weights of the substances which at that time had been well determined could be represented by multiples of the atomic weight of hydrogen. Prout had so little faith in the exactness of his hypothesis that he published his paper under the veil of anonymity. Whatever may be the opinion one holds about this hypothesis, whatever fate may be reserved for it in the future, it is impossible not to pay homage to the rare penetration of its author. Right or wrong, it permitted him to divine the specific weight of hydrogen forty years before it was determined experimentally with any degree of accuracy.

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* [From *Bulletin de l'Académie Royale de Belgique* [2] **10** (1860), 208-336. (Portions translated, pp. 208-213, and p. 336)].

From the point of view of the philosophy of nature the import of Prout's idea is immense. Those components of compound substances which we regard as elementary on account of their absolute immutability for us, would themselves be only compounds. Such elements, whose discovery is the glory of Lavoisier and has immortalised his name, can thus be considered as being derived from the condensation of a unique substance: we are thus naturally conducted to the unity of matter, although we in fact observe its plurality, its multiplicity.

In England the hypothesis of Dr Prout was almost universally accepted as absolute truth. The work executed by Professor Thomas Thomson of Glasgow in order to base it on analytical experiments, greatly contributed to this result. Nevertheless, the same thing did not hold for Germany or France. The immense prestige which surrounded the name of Berzelius and the legitimate confidence inspired by his work on the weights of the atoms were incontestably the cause of this. Even in England doubts arose: as early as 1833 Professor Turner, on the invitation of the British Association for the Advancement of Science, undertook a series of analyses, from which he drew the conclusion that the hypothesis of Dr Prout was not exact.* In

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* [Phil. Trans. for 1833, 523-544.]

1839, Professor Penny of Glasgow arrived at the same conclusion,[*] although his results differed in some points from those obtained by Turner. The determination of the atomic weight of carbon made by M. Dumas and myself in 1839-40 called the attention of chemists anew to this subject.[†] The atom of carbon deduced from our syntheses of carbonic acid agrees in fact entirely with Prout's hypothesis. The new syntheses of water which M. Dumas published in 1843,[‡] and which were confirmed by the work of MM. Erdmann and Marchand, led to the same result.

In 1842 and in 1843,[§] M. de Marignac of Geneva undertook a series of researches on chlorine, bromine, iodine, nitrogen, silver, and potassium for the purpose of submitting Prout's law to a new and careful examination.[||] It has been shown in the most certain fashion by the Genevan chemist, whose accuracy is generally recognised, and to whose skill and conscientiousness Berzelius has paid a justly merited tribute, that the unit adopted by Prout is twice too great as far as chlorine is concerned. But he declared himself to be of the firm opinion that taking into account the extreme difficulty of experimentally attaining results of absolute exactness, we cannot consider as contrary to Prout's law the atoms he has found for silver, potassium, bromine, iodine, and nitrogen. Thus, according to M. de Marignac, the principle may be exact, only the unit should be diminished by half.

At the end of 1857 M. Dumas published a *Memoir on the Equivalents of the Elements.*[¶] As might be expected this memoir produced a great sensation. The illustrious French chemist, taking as basis M. de Marignac's researches on silver, found that all well known substances which he had occasion to examine, perfectly conform to the principle of Prout, when certain modifications are applied to this principle. According to him, the elements are multiples of hydrogen by 1, or by 0·5, or finally by 0·25. My illustrious master accompanied his work by philosophical considerations which though very important have no connection with the question I propose to treat.

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[*] [Phil. Trans. for 1839, 13-33.]

[†] [Ann. chim. phys. [3] **1** (1841), 5-38.]

[‡] [*Ibid.* [3] **8** (1843), 189-207.]

[§] [J. pr. Ch. **26** (1842), 461-478.]

[||] [C. R. **14** (1842), 570-573 ; Bibl. Univ. **46** (1843), 350-377.]

[¶] [Ann. chim. phys. [3] **55** (1859), 129-210.]

Such, at the present time, is the state of knowledge regarding the relations between the atomic weights of the elements.

For a great number of years I have dedicated all my leisure to elucidate this problem. I confess frankly that when I undertook these researches, I had an almost absolute confidence in the exactness of Prout's principle. The doubt at which I had hinted in my work on the atom of carbon, in 1845,* had its origin in the result of two determinations which were in poor agreement with my other syntheses.

In my investigations I have dealt with chlorine, bromine, fluorine, sulphur, nitrogen, potassium, sodium, lithium, calcium, barium, lead, and silver. In the course of the long and laborious researches to which I have devoted myself, it may easily be conceived that I obtained successively the most discordant results, according to the substances and methods I employed. Sometimes these results were in absolute agreement with the principle of Prout: this was the case for example with lead, silver, sodium, and calcium determined as a function of the atom of carbon; sometimes they were completely irreconcilable with that law: such was

* [Brux. Acad. Sci. Bull. **16** (1849), 33.]

the case of lead determined as a function of the atom of nitrogen and of sulphur; of silver determined as a function of nitrogen and of chlorine; of potassium determined with regard to oxygen and chlorine.

I dare affirm without fear of being contradicted that any chemist who has pursued research on the weights of the atoms, *if he has varied his methods*, if he has determined the weight of the atom of one substance as a function of the weight of the atom of two or three different substances, has encountered the same difficulties, the same contradictions. I accordingly experienced for long many a painful perplexity.

However, as I lately intimated to the Academy in requesting it to take note of my declaration, for some time all doubt has vanished from my mind. I have reached the complete conviction, the entire certainty, as far as certainty can be attained on such a subject, that Prout's law, with all the modifications due to M. Dumas, is nothing but an illusion, a pure hypothesis expressly contradicted by experiment. Chemists after examining the work which I have the honour of now presenting in detailed analysis to the Academy, if they can cast away their prejudices and mental prepossessions, and place their reliance on experiment, will soon share my conviction, namely, that there does not exist a common divisor for the weights of the elements which unite to form all definite compounds.

The paper which I now publish only embodies my researches on *nitrogen*, *chlorine*, *sulphur*, *potassium*, *sodium*, *lead*, and *silver*. I chose these substances because they are the best known, form the stablest compounds, and because generally they have been regarded as obeying Prout's law. I have sufficiently emphasised that my aim was not to determine the weight of the atom of these substances, but rather the ratios of the weights of the atoms: in order to see if a common divisor exists for these ratios I have employed methods which in my opinion would most surely lead to a definite result. Whilst varying the methods I have preferred as far as possible to adopt those already employed by chemists recognised for their proved accuracy. This I did in order to obtain a more efficacious control. It is clearly evident that if results repeated sufficiently often agree with those previously obtained, the probability in favour of their exactness becomes very great; if on the contrary they differ, it is possible from the thorough study of all the conditions of experiment to find the means of assuring oneself on what side the truth lies. In this way I have succeeded in discovering errors which otherwise would have undoubtedly escaped me.

Although I only aimed at determining the ratios of numbers, I have nevertheless made two determinations, either of which would at once permit the deduction from all my experiments of the atom of these seven elements relatively to oxygen.

We shall see later that the weights of these atoms are in close accordance with those generally accepted, save in the case of nitrogen.

The determinations of the ratios have been made by way of *synthesis*, or by *double decomposition*. I have only had recourse to *analysis* to procure the data necessary for the calculation of the atomic weights as a function of oxygen.

[The details of Stas's experiments come in here. The ratios to which the experiments lead are quoted by Marignac in the "Commentary" which follows this paper (see p. 48), and are not given here. The last page of Stas's discussion follows.]

If we cast our eyes on the atomic weights of ammonium and nitrogen * we see that they differ by 4·02 instead of 4. From this it undubitably follows either that my syntheses of nitrate of silver are inaccurate and that the quantity of this salt produced from metallic silver is a little higher than what I found, which removes me still further from Prout's law, or else that the atomic weight of hydrogen itself is in error by 1/200 of its value.

My researches as a whole lead me to believe that the error exists rather in the atomic weight of hydrogen than in that of nitrogen.

If this opinion, to which with all reserve I would direct the attention of chemists, is correct—and I mean soon to investigate the point by carrying out the synthesis of water by a new method—it follows that the basis on which Dr Prout had erected his law, is itself without foundation.

Whatever doubt I raise with regard to the accuracy of the atomic weight of hydrogen being represented by 1, oxygen being 8, there can remain no doubt concerning the principle itself. I conclude then by saying: as long as we hold to experiment for determining the laws which regulate matter, we must consider Prout's law as a pure illusion, and regard the undecomposable bodies of our globe as distinct entities having no simple relation by weight to one another. The incontestable analogy of properties observed amongst certain elements must be sought in other causes than those originating in the ratio of weight of their reacting masses.

* [The figures are:—Ammonium, 18·06; nitrogen, 14·04.]

COMMENTARY ON THE FOREGOING PAPER, BY C. M[ARIGNAC].

RESEARCHES ON THE MUTUAL RELATIONS OF ATOMIC WEIGHTS, BY J. S. STAS*

(Bulletin de l'Acad. Royale de Belgique, 2nd Séries, Vol. x., No. 8.)

M. STAS has just published a résumé of the researches to which he has devoted himself for a great number of years, researches made with the object of verifying whether simple relations really exist amongst the atomic weights of various elements.

Through the determination of the atomic weight of carbon made in 1839 and 1840 conjointly with M. Dumas,† he was initiated into the difficulties of such work and the minute precautions necessary for arriving at rigorously exact results, and he has neglected nothing to give these new researches every requisite degree of accuracy. He has thought too, and rightly thought, that it was not enough to have adopted all these precautions; he has described them in detail in the account of his experiments in order that every chemist should be in a position to judge of the degree of confidence to be accorded to the results he has obtained.

We must signalise this memoir, not only because of the importance of the subject treated, but also for the numerous lessons it affords to chemists who wish to devote themselves to work requiring extreme accuracy. They will find in it most valuable instructions and a model to follow.

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* [From *Bibliothèque Universelle* (*Archives*), **9** (1860), 97-107. Marignac uses the same title as Stas and the reader might suppose that the paper was by Stas except for the contents and the initials "C. M." at the end. The whole paper is here translated.]

† [C. R. **11** (1840), 991-1008; Ann. Chim. Phys. [3] **1** (1841), 5-38.]

But we cannot in this extract linger over these details, which should be read in the memoir of the author, and we must content ourselves with discussing the principal results at which he has arrived.

Although these researches have been extended to a considerable number of elements, the memoir cited only contains those relative to chlorine, sulphur, nitrogen, silver, potassium, sodium, and lead, these elements having been chosen as the best known, forming the most stable compounds, and generally because they have been considered as obeying Prout's law. The aim of the author was not so much to determine their atomic weights as to ascertain by the study of the most sharply defined actions that can be carried out between them, if there exists amongst these weights the simple ratios assumed by Prout's law.

To attain this end the author has performed the synthesis of the chloride, sulphide, and nitrate of silver, of the nitrate and sulphate of lead, the analysis of chlorate of potash and of sulphate of silver, and finally he has determined the ratios of silver to the chlorides of potassium, sodium, and ammonium, and those of nitrate of silver to the chlorides of potassium and ammonium. Each of these determinations has been made as far as possible by several different methods, and in every case with the aid of products prepared or purified by different procedures described with all necessary detail.

The results arrived at by the author in these twelve series of determinations are summarised in the following table. The table contains the gravimetric ratios of the two substances compared in each series, confronted with the ratio calculated from Prout's hypothesis, and in addition the record of the maximum and minimum values obtained in the various series, so that the reader can judge from the deviation of these two figures, to what extent the differences between the experimental results and the calculated values can be attributed to errors of observation. The calculation has been made by adopting the number 35·5 for chlorine and 103·5 for lead.

$Ag : Cl = 100$:	min.	32·841		
	max.	32·850		[M. 32·854] *
	mean	32·8445	(calc. 32·870)	
$Ag : S = 100$:	min.	14·849		
	max.	14·854		
	mean	14·852	(calc. 14·814)	
$Ag : AgO,NO_5 = 100$:	min.	157·463		
	max.	157·481		[M. 157·455]
	mean	157·473	(calc. 157·404)	
$Ag : KCl = 100$:	min.	69·099		
	max.	69·107		[M. 69·098]
	mean	69·103	(calc. 68·981)	
$Ag : NaCl = 100$:	min.	54·206		
	max.	54·209		
	mean	54·2078	(calc. 54·166)	
$Ag : NH_4Cl = 100$:	min.	49·590		
	max.	49·600		[M. 49·556]
	mean	49·5944	(calc. 49·537)	
$AgO,NO_5 : KCl = 100$:	min.	43·864		
	max.	43·885		[M. 43·878]
	mean	43·876	(calc. 43·823)	
$AgO,NO_5 : NH_4Cl = 100$:	min.	31·486		
	max.	31·490		
	mean	31·488	(calc. 31·470)	

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* [The figures in square brackets were obtained by Marignac at an earlier date. They are quoted by him in a footnote at p. 99 of the Commentary. Compare Bibl. Univ. **46** (1843), 350-373.]

$$\mathrm{Pb : PbO,NO_5 = 100 :} \begin{cases} \text{min. } 159{\cdot}959 \\ \text{max. } 159{\cdot}982 \\ \text{mean } 159{\cdot}969 \quad \text{(calc. } 159{\cdot}903\text{)} \end{cases}$$

$$\mathrm{Pb : PbO,SO_3 = 100 :} \begin{cases} \text{min. } 146{\cdot}419 \\ \text{max. } 146{\cdot}443 \\ \text{mean } 146{\cdot}427 \quad \text{(calc. } 146{\cdot}376\text{)} \end{cases}$$

$$\mathrm{KO,ClO_5 : KCl = 100 :} \begin{cases} \text{min. } 60{\cdot}838 \\ \text{max. } 60{\cdot}853 \qquad \qquad [\text{M. } 60{\cdot}839] \\ \text{mean } 60{\cdot}846 \quad \text{(calc. } 60{\cdot}8163\text{)} \end{cases}$$

$$\mathrm{AgO,SO_3 : Ag = 100 :} \begin{cases} \text{min. } 69{\cdot}197 \\ \text{max. } 69{\cdot}209 \\ \text{mean } 69{\cdot}203 \quad \text{(calc. } 69{\cdot}230\text{)} \end{cases}$$

We see that the differences between the results obtained by M. Stas and those which Prout's law requires, although inconsiderable, are yet very much greater (six to eight times, and in two cases even thirteen or fourteen times greater) than the greatest differences between the results found in each series of experiments.

On the basis of these observations M. Stas calculates for the elements with which he has experimented, the following atomic weights referred to that of oxygen as 8. I place beside them the numbers which I deduced from my experiments of 1843 for some of the same elements, and also the numbers adopted by the partisans of Prout's law.

	Stas.	Marignac.	Prout.
Silver	107·943	107·921	108
Chlorine	35·46	35·456	35·5
Potassium	39·13	39·115	39
Sodium	23·05	...	23
Ammonium	18·06	...	18
Nitrogen	14·04	14·02	14
Sulphur	16·037	...	16
Lead (from sulphate) . . .	103·453	...	103·5
Lead (from nitrate) . . .	103·460	...	103·5

The atomic weight of silver has been derived in this calculation from all the experiments involving this metal, chlorine, and potassium, to which oxygen is related by the analysis of chlorate of potash. But it may also be obtained by starting from another series of experiments completely independent of these, namely from the synthesis of the sulphide of silver and the analysis of sulphate of silver. We then find

Silver . . .	107·924
Sulphur . .	16·029

The difference between these numbers and those of the first table shows what is the probable magnitude of the error by which these values are affected.

M. Stas observes that there results from his experiments a difference between the atomic weights of NH_4 and of nitrogen which is equal to 4·02 instead of 4. He does not believe that this difference can result from the imperfections of the experimental methods; he concludes that the ratio of the atomic weights of hydrogen and oxygen is not exactly 1 : 8, and proposes to submit this question to further study. This is perhaps exaggerating a little the degree of confidence to be placed in determinations of this kind, for the difference does not greatly exceed that which exists between the atomic weight of sulphur obtained by the author in two distinct series of experiments.

If I have recorded alongside the numbers of M. Stas those which I had previously obtained, it is not merely for the purpose of drawing attention to their close agreement; it seems to me that an important conclusion may be drawn from them. I recognise fully, after having studied the splendid work of this savant, that he has exercised in his experiments infinitely greater care than I thought to be necessary not only in the purification of the substances used in the researches, but also in the accuracy of his weighings, and in taking all imaginable precautions for the purpose of eliminating errors. His results therefore offer much greater guarantees of accuracy than mine; yet we see how little they differ from them, and it is specially noticeable that in the mean they are no nearer than mine to the numbers calculated from Prout's law. It seems to me permissible to conclude that if, after fresh improvements have been made in the methods of purification of the substances or in the experimental methods, some chemist at a future date takes up the same series of experiments with still greater guarantees of accuracy, the difference which may be found between his results and those of M. Stas will very probably be of the same order as that which exists between the latter and my own, and that no greater accordance with Prout's law will be found.

This being my opinion on the question, it may perhaps be found astonishing that I do not entirely agree with the conclusions of M. Stas that "we must consider Prout's law as a pure illusion, and regard the undecomposable bodies of our globe as distinct entities having no simple relation by weight to one another." I may be permitted some observations on these conclusions which appear to me to be too absolute; they will bear on two separate points.

First, I confess that I shall not be convinced of the accuracy of an atomic weight determination (or rather, I shall not be able to form a clear opinion of the degree of confidence to be accorded to it) unless this weight has been obtained by several absolutely independent methods, based on the analysis of a number of compounds altogether distinct from one another. I recognise that this may be a very troublesome condition to fulfil, but I believe it to be a point which should above all be attended to by chemists who desire to work anew at these difficult questions. Even in the experiments of M. Stas I see two methods of arriving at the atomic weight of silver; one gives 107·943, the other 107·924. But that is not all. I should like, for example, that this savant, exercising all the care and perspicacity which he devoted to his researches, might take up the analysis of the silver salts of organic acids which gave me the figure 107·968 as the atomic weight of silver.* Perhaps he might find yet other methods of arriving at the same end, and we should then see if the results yielded by the various methods differ from one another by a less amount than the differences found between these results and those calculated by means of Prout's hypothesis.

I expressly add that by different methods, I mean methods which depend on the analysis or synthesis of absolutely distinct compounds, and not merely those which differ only in the means of bringing the same substances into chemical action. Thus when in my first research I invoked as a proof of accuracy the coincidence of the ratio observed between silver and chloride of potassium on the one hand, with, on the other, the same ratio calculated from other experiments giving first the direct ratio of chlorine to silver, and second that between chloride of silver and chloride of potassium, or when M. Stas invokes as a control of the synthesis of nitrate of silver the experiments by which he determined the ratio between this nitrate and chloride of silver, which is itself directly connected with silver, I only recognise in these a confirmation of the exactness with which the experiments were made, and in no wise a confirmation of the experimental method itself. Indeed, if for any reason the nitrate of silver prepared under normal conditions does not contain its elements rigorously in the proportion of their atomic weights, the most exact methods applied to its analysis or its synthesis will show the same error in the ratio of these weights.

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* *Bibl. Univ.* 1846 (*Archives*), vol. 1, p. 57.

This is indeed the principal cause of the doubt which still exists in my mind. I do not regard it as absolutely demonstrated that many compounds do not contain, constantly and normally, an excess of one of their elements, an excess doubtless very minute, but still sensible in very delicate experiments. To make this idea clear I will cite a case in which this tendency is shown, though only to such a degree that it could scarcely pass unrecognised.

It has long been held that monohydrated sulphuric acid* is a perfectly stable compound, as might be expected from the powerful affinity of its two components. Yet I have shown † that it is on the contrary not at all stable. The slightest rise of temperature leads to the disengagement of the vapours of anhydrous sulphuric acid, and only when it has been brought by this process to contain a slight excess of water (about 1 per cent.) does it become perfectly stable and unaltered by distillation.

Are we justified in affirming that it is not in the same way a normal condition, so to speak, of the existence of a compound, one of whose components is very volatile or even gaseous, always to contain an excess, often perhaps scarcely appreciable, of the fixed component, the affinity of that free portion being necessary to counterbalance the elasticity of the gaseous substance?

Or perhaps conversely, just as hydrated sulphuric acid retains about 300 degrees a slight excess of water, which is itself vaporisable at 100 degrees, may it not be that a compound such as the sulphide or nitrate of silver should invariably contain, even at very elevated temperatures, a slight excess of sulphur or of nitric acid?

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* [Marignac means what we should now call simply sulphuric acid (HO,SO_3 in the contemporary notation).]

† *Bibl. Univ.* 1853 (*Archives*), vol. 22, p. 225.

Lastly, are we sure, when we weigh a substance, that we have obtained really and uniquely the weight of that substance? We know that fused silver and fused litharge retain in solution a perceptible amount of oxygen. We assume that they lose it completely at the moment of solidification, but I do not believe that anyone has ever assured himself of this by rigorous experiment; and in any case this has not been done for all other substances. Even less are we assured of the impossibility of their having condensed atmospheric nitrogen.

These possible causes of error, to which we could probably still add others, lead me, although I am satisfied that the experiments of M. Stas are perfectly exact, to be not absolutely convinced that the differences observed between his results and those required by Prout's law cannot be explained by the imperfect character of the experimental methods.

But assuming now that these objections are without foundation and that the experiments give us in reality the ratios of the atomic weights of the elements, there remains another objection which prevents me from concluding from them that Prout's law is nothing but a pure illusion, and that the elements are entities necessarily distinct.

One need, in fact, only glance at these weights to see that if they do not coincide absolutely with the numbers of Prout, they are so close to them that it is impossible to consider this fact as accidental. Thus for the nine determinations resulting from this work of Stas, the difference is as a mean 0·056, say 1/18 of the equivalent of hydrogen, or 1/9 of the half-equivalent. It is known besides that a concordance at least equal is exhibited for other elements whose atomic weights seem to have been determined with some certainty, such as iron, calcium, carbon.

We may thus say of Prout's law what must be said of the laws of Mariotte and of Gay-Lussac regarding variations in gaseous volumes. These laws, for long considered absolute, have been recognised as inexact when the experiments have been carried out with the degree of precision attained by M. Regnault, M. Magnus etc. Nevertheless they will always be considered as expressing natural laws not only from the practical point of view, since they allow us to calculate in most cases with a sufficient approximation the changes in volume of gases, but even from the theoretical point of view, for they very probably express the normal law of these changes of volume, apart from certain disturbing influences whose effect we shall perhaps also be able at a later date to compute.

We may believe that it is the same with Prout's law: even if it is not rigorously confirmed by experience, it none the less appears to express the ratios between the atomic weights of the elements with sufficient accuracy for the practical calculations of chemistry and perhaps also the normal ratios which should exist between these weights, apart from some perturbing causes the elucidation of which may in future exercise the sagacity or the imagination of chemists.

While preserving the fundamental principle of that law, that is to say, while adopting the hypothesis of the unity of matter, could we not make for example the following supposition, to which I do not otherwise attach importance except as showing that we might explain the discordance that appears to exist between the results of observation and the immediate consequences of that principle? Could we not suppose that the cause (unknown but probably different from the physical and chemical agencies familiar to us) which has determined certain groupings of the atoms of the sole primordial matter so as to give rise to our chemical atoms, by impressing on each of these groups a special character and particular properties, should not at the same time have exercised an influence on the manner according to which these groups of primordial atoms would obey the law of universal attraction, in such wise that the weight of each group might not be exactly the sum of the weights of the primordial atoms composing it?

To conclude, I must not forget an important observation due to the illustrious chemist who has so forcibly called attention to these interesting questions. The fundamental principle which led Prout to formulate his law, namely the idea of the unity of matter, and all the more or less brilliant conceptions which have been based on this principle, are altogether independent of the magnitude of the unit which serves as common divisor to the atomic weights of the elements, and which might therefore be considered as expressing the weight of the atoms of the primordial matter. Whether this weight be that of a single atom of hydrogen, or of a half or a quarter atom or whether it be an infinitely smaller fraction, say a hundredth or a thousandth, all these considerations would none the less preserve for it the same degree of probability. There would only result less simple ratios of composition amongst the various elementary components. C. M.

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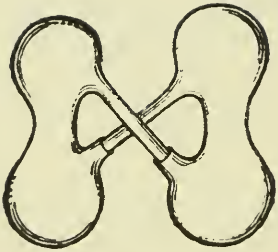

PREFACE

THE two papers here translated from the French appeared in Volume 46 of the Comptes Rendus de l'Académie des Sciences. The one entitled "Sur une Nouvelle Théorie Chimique" was a short note, preliminary to the full paper bearing the same title, and it appeared in French only. The paper entitled "Recherches sur L'Acide Salicylique" differs in some material respects from the English one entitled "Researches on Salicylic Acid" and hence it appeared desirable to reprint the latter as well as a translation of the former. The French version must have left Couper's hands before the English one, and between the respective dates of their publication Couper decided to make the change from C = 6 to C = 12.

Of the full paper "On a New Chemical Theory," there is a French version as well as the English one. The former appears to have been drawn up at a slightly later date than the latter, since in it the change from the dotted lines used in Couper's earlier formulæ to continuous lines has been made throughout. The French version includes certain paragraphs that do not occur in the English paper. These have been translated and introduced, enclosed within square brackets, at their respective places. A few typographical errors, occurring in the original papers and confined almost exclusively to the extended formulæ, have been corrected.

L. D.

INTRODUCTION

Archibald Scott Couper shares equally with August Kekulé the credit for enunciating the theoretical conception of the linking of carbon atoms in the molecules of organic compounds. His views upon this subject were formulated practically simultaneously with those of Kekulé, but after the MS. of the first version of his paper "On a New Chemical Theory"* had left his hands, the publication of the paper was unduly delayed as a consequence of circumstances that were beyond his control. These circumstances are described in a communication submitted to the Royal Society of Edinburgh in 1909† by Professor Richard Anschütz, Kekulé's successor at the University of Bonn. It appears from the story as narrated by Anschütz, that Couper, who was a student in Wurtz's laboratory in Paris, handed his paper to Wurtz for submission to the Paris Academy; that Wurtz, who was not a member of the Academy at the time, had to pass it on to a member for presentation and for some reason was dilatory in doing this; and that in consequence of the delay thereby occasioned, Couper suffered the disappointment of finding himself anticipated—although by a few weeks only—by the appearance of the famous paper "On the Composition and Metamorphoses of Chemical Compounds and on the Chemical Nature of Carbon" in which Kekulé dealt with the same subject.* Anschütz shows in his paper that Couper's views were arrived at entirely independently and also that, had it not been for the delay referred to, they might have been published as early as Kekulé's. The accuracy of the narrative that Anschütz gives is fully established by communications that he quotes from Lieben, who was a fellow-student with Couper in Wurtz's laboratory, and from Ladenburg, who obtained his information from Wurtz himself.

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* Here reprinted at p. 9 in translation from the French of the Comptes Rendus de l'Académie des Sciences.

† Proc. Roy. Soc. Edin., **29** (1909), 200.

It is known that the misfortune of having been forestalled in publication by Kekulé caused Couper intense mortification and it is not improbable that the shock thereby communicated to his sensitive nature may have contributed in some measure to the subsequent mental discomposure that clouded his life while still a young man and led to his withdrawal from active chemical research and to his residing during the remainder of his life in retirement and comparative seclusion in his native town of Kirkintilloch. He died there in 1892 in his sixty-first year.

Besides the independent announcement of the linking of carbon atoms, there are some other matters connected with Couper's publications that deserve more particular notice :—

Examples of formulæ in which connecting lines—at first dotted, afterwards continuous—between the separate symbols, to indicate the relationships of the atoms within molecules, are met with for the first time in the papers "On a New Chemical Theory," so that Couper was the originator of the idea of representing the "structure" (Butlerow) or "constitution" (Erlenmeyer) of molecules by means of formulæ.

The general expressions that Couper suggested for representing the composition of hydrocarbons (pp. 10 and 25) are not at first sight quite easy to follow, while some slight confusion is introduced by the employment, to begin with, of $n\mathrm{C}^2\mathrm{M}^4$ (with $\mathrm{C}=6$) and later of $n\mathrm{CM}^4$ (with $\mathrm{C}=12$). These expressions, as Anschütz has pointed out, were misunderstood by both Kekulé and Butlerow. It seems to be beyond doubt that by $n\mathrm{CM}^4$ Couper meant n carbon atoms, each with its four "combining powers" wholly engaged in single union with carbon or hydrogen, that is, what is met with in the "saturated" or paraffin hydrocarbons. On the other hand, by $m\mathrm{M}^2$ he evidently wished to express m times the degree of "non-saturation" that is associated with a double union of one carbon atom with another (in a "double bond").

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* Annalen, **106** (1858), 129.

Couper employed a few unusual terms in those of his papers that were published in English journals. With a view to preserving uniformity, these have been adopted in the translations from the French.

It was largely owing to the circumstance that the experiments of Couper on the action of phosphorus pentachloride on salicylic acid (upon which doubt had been cast consequent on the failure of Kekulé, Kolbe, and others to confirm his results) were found to be quite correct by Anschütz, that the latter instituted enquiries which led, as the result of prolonged and persistent efforts made by the late Professor Crum Brown, to the tracing of the ancestry and relatives of Couper and the collection of much interesting information concerning his student and later career. A sympathetic biographical notice of Couper together with a critical review of his papers is included in the paper by Anschütz already noticed. Particulars connected with the unveiling of a memorial plaque at his birthplace at Townhead, Kirkintilloch, on 9th October 1931, are printed in

Volume 50 of the Journal of the Society of Chemical Industry (pp. 383-4 and 931-5). The inscription on the plaque reads:—

THIS PLAQUE MARKS THE BIRTHPLACE OF
BORN 1831 ARCHIBALD SCOTT COUPER DIED 1892
WHOSE BRILLIANT PIONEERING CONTRIBUTIONS
TO CHEMICAL THEORY HAVE WON FOR HIM INTERNATIONAL
RENOWN, AND WHOSE GENIUS, STIFLED BY AN EARLY ILLNESS
WAS DENIED THE OPPORTUNITY OF CONSUMMATION

ERECTED BY PUBLIC SUBSCRIPTION ON THE
OCCASION OF THE CENTENARY OF HIS BIRTH
31ST MARCH 1931

ON A NEW CHEMICAL THEORY.*

(NOTE PRESENTED BY M. DUMAS.)

I HAVE the honour to lay before the Academy the principal features of a new chemical theory that I propose for organic combinates.

I go back to the elements themselves, of which I study the mutual affinities. This study is, in my opinion, sufficient for the explanation of all chemical combinates, without it being necessary to revert to unknown principles and to arbitrary generalizations.

I distinguish two species of affinity, namely:

1°. Affinity of degree; 2°. Elective affinity.

By affinity of degree, I mean the affinity that one element exerts upon another with which it combines in several definite proportions. I call elective affinity that which different elements exert with different intensities upon one another. Taking carbon for example, I find that it exerts its combining power in two degrees. These degrees are represented by CO^2 and CO^4, that is to say by oxide of carbon and carbonic acid, adopting for the equivalents of carbon and of oxygen the numbers 12 and 8.

So far as concerns its elective affinities, carbon differs from the other elements and exhibits, so to speak, a special physiognomy. The features that characterise this elective affinity of carbon are the following:

1°. It combines with equal numbers of equivalents of hydrogen, of chlorine, of oxygen, of sulphur, etc., which can mutually replace one another so as to satisfy its combining power.

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* [From Comptes Rendus, **46** (1858), 1157-1160.]

2°. It enters into combination with itself.

These two properties suffice, in my opinion, to explain all that is presented as characteristic by organic chemistry. I believe that the second is pointed out here for the first time. In my opinion it accounts for the important and still unexplained fact of the accumulation of molecules of carbon in organic combinates. In these compounds where 2, 3, 4, 5, 6, etc., molecules of carbon are bound together, it is carbon which serves as link to carbon.

It is not hydrogen that can bind together the elements of organic bodies. If, like carbon, it had the power to combine with itself, it would be possible to form the compounds H^4Cl^4, H^6Cl^6, H^8Cl^8.

So far as oxygen is concerned, I admit that an atom of this body in combination exerts a powerful affinity upon a second atom of oxygen that is itself combined with another element. This affinity is modified by the electrical position of the elements to which the atoms of oxygen are respectively attached. The following explanations will make this conception understood.

The highest combining power known for carbon is that of the second degree, that is to say 4.

The combining power of oxygen is represented by 2.

All the combinates of carbon can be referred to two types. One of these is represented by the symbol

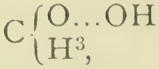
$$nCM^4,$$

the other by the symbol

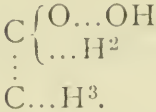
$$nCM^4 - mM^2$$

where m is $< n$, or else $nCM^4 + mCM^2$, where n can become nil. As examples of the first type, the alcohols, the fatty acids, the glycols, etc., may be cited.

Methylic and ethylic alcohols will be represented by the formulæ



$$C\begin{cases}O\ldots OH\\ H^3,\end{cases}$$

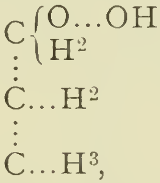


$$\begin{array}{l} C\begin{cases}O\ldots OH\\ \ldots H^2\end{cases}\\ \vdots\\ C\ldots H^3.\end{array}$$

It will easily be seen that for methylic alcohol the limit of combination of the carbon is equal to 4, the carbon in it being combined with 3 of hydrogen and with 1 of oxygen. This oxygen, of which the combining power is equal to 2, is in turn combined with another atom of oxygen, itself united to 1 of hydrogen.

In the case of ordinary alcohol, each of the two atoms of carbon satisfies its combining power, on the one hand, by uniting with 3 atoms of hydrogen or of hydrogen and oxygen, and, on the other hand, by uniting with the other atom of carbon. The oxygen is combined in the same manner as in the preceding example. In these cases it will be seen that the carbon belongs to the first type, each atom being combined in the second degree.

In propylic alcohol,

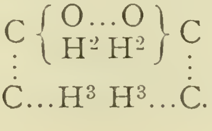


$$\begin{array}{l} C\begin{cases}O\ldots OH\\ H^2\end{cases}\\ \vdots\\ C\ldots H^2\\ \vdots\\ C\ldots H^3,\end{array}$$

the combining power of the atom of carbon that is situated in the middle is reduced to 2 for hydrogen, since it is combined chemically with each of the two other atoms of carbon.

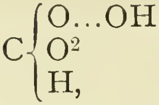
Formulæ analogous to those preceding, express the constitution of the other alcohols.

The constitution of ether is represented by the formula



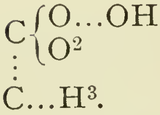
$$\begin{array}{ccc} C & \left\{\begin{matrix}O\ldots O\\ H^2\;H^2\end{matrix}\right\} & C\\ \vdots & & \vdots\\ C\ldots H^3 & & H^3\ldots C.\end{array}$$

Formic acid is



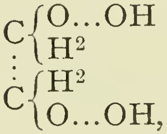
$$C\left\{\begin{matrix} O\ldots OH \\ O^2 \\ H, \end{matrix}\right.$$

acetic acid



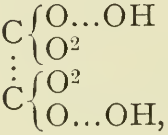
$$\begin{array}{l} C\left\{\begin{matrix} O\ldots OH \\ O^2 \end{matrix}\right. \\ \vdots \\ C\ldots H^3. \end{array}$$

The constitution of glycol is represented by the formula



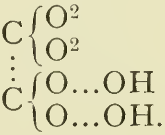
$$\begin{array}{l} C\left\{\begin{matrix} O\ldots OH \\ H^2 \end{matrix}\right. \\ \vdots \\ C\left\{\begin{matrix} H^2 \\ O\ldots OH, \end{matrix}\right. \end{array}$$

that of oxalic acid by the formula



$$\begin{array}{l} C\left\{\begin{matrix} O\ldots OH \\ O^2 \end{matrix}\right. \\ \vdots \\ C\left\{\begin{matrix} O^2 \\ O\ldots OH, \end{matrix}\right. \end{array}$$

or, if it is desired to join the negative oxygen to one of the poles of the molecule, by the formula



$$\begin{array}{l} C\left\{\begin{matrix} O^2 \\ O^2 \end{matrix}\right. \\ \vdots \\ C\left\{\begin{matrix} O\ldots OH \\ O\ldots OH. \end{matrix}\right. \end{array}$$

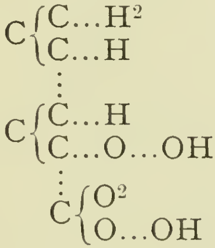
Be that as it may, however, it can be seen according to this theory that, in the constitution of organic acids of the first type, the presence of 2 atoms of oxygen combined together in such a manner that both are attached directly to carbon and situated near the negative oxygen—that is to say, near the oxygen which carries along with it the oxygen raised to an electro-positive state by its combination with one atom of a relatively electro-positive element; that the presence, I say, of these atoms of oxygen is necessary in order that the negative oxygen may find itself in that electrical state which gives to the body the properties generally described by the name of *acids*.

This is a particular case of a general law; because it can be seen, according to this theory, how the electro-positive or electro-negative value of the elements mutually modifies and conditions the electro-positive or electro-negative value of the other elements.

This law differs from the electric hypothesis that chemists have hitherto defended, but which has never been able to receive a complete application to their views on organic chemistry; that, on the contrary, which I advance, agrees perfectly with the application of the theory that I propose, to the facts.

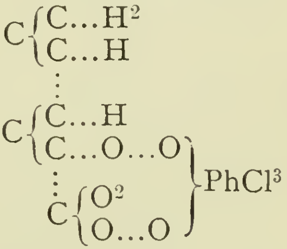
There remains nothing for me but to add the manner in which I formulate salicylic acid and the terchlorophosphate of salicyl which I made known in a communication submitted to the Academy at its last sitting.

Salicylic acid.



$$\begin{array}{l} C\begin{cases}C\ldots H^2\\ C\ldots H\end{cases}\\ \quad\vdots\\ C\begin{cases}C\ldots H\\ C\ldots O\ldots OH\end{cases}\\ \quad\vdots\\ \quad C\begin{cases}O^2\\ O\ldots OH\end{cases}\end{array}$$

Terchlorophosphate of salicyl.



$$\begin{array}{l} C\begin{cases}C\ldots H^2\\ C\ldots H\end{cases}\\ \quad\vdots\\ C\begin{cases}C\ldots H\\ C\ldots O\ldots O\end{cases}\\ \quad\vdots\\ \quad C\begin{cases}O^2\\ O\ldots O\end{cases}\end{array}\Bigg\}PhCl^3$$

These formulæ suffice, for the moment, to indicate my ideas on the constitution of the bodies.

ON A NEW CHEMICAL THEORY.*

THE end of chemistry *is its theory.* The guide in chemical research *is a theory.* It is therefore of the greatest importance to ascertain whether the theories at present adopted by chemists are adequate to the explanation of chemical phenomena, or are, at least, based upon the true principles which ought to regulate scientific research.

Among those which have lately been developed, there is one, on account of its apparently numerous merits, which particularly claims investigation, and respecting which we deem that it would not be unprofitable were either new proofs of its scientific value furnished, or, on the contrary, should considerations be adduced establishing not only its inadequacy to the explanation, but its ultimate detriment to the progress of science. I allude to the system of types as advocated by Gerhardt.

This system, striking alike for the breadth of its conception, and the logical and consequent manner in which it has been developed, has been controverted from the point of view afforded by theories less far-reaching than the one under consideration, and even based upon a one-sided and restricted appreciation of certain chemical reactions. The consequence is that this opposition has not impaired the favour with which the unitary system has been received, but has rather tended to display it in a more advantageous light.

Imposing as this theory is, it is nevertheless all the more necessary to submit it to a strict investigation; for there is nothing so prejudicial in the search for truth as the blind spirit of conservation. A rational belief demands the test of a preliminary doubt.

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* [From *Phil. Mag.* [4] 16 (1858), 104-116.]

There are two conditions which every sound theory must fulfil:—

1. It must be proved to be empirically true.
2. It must no less be philosophically true.

I admit that this theory is for the most part empirically true, that is to say, it is not contradicted by many of the facts of the science. Evidence that this condition is only partially fulfilled, is to be found—

1. In the circumstance that the peroxides, for instance, do not fit very satisfactorily into the types.

2. The principle of double decomposition cannot well be applied to the conversion of the anhydrous sulphuric acid into the hydrate of that acid by the action of one equivalent of water, the formulæ of these bodies being, according to Gerhardt, in their free state $O.SO^2$ and H^2O. Combined, they become simply SH^2O^4.

The same remark applies in like manner to carbonic acid. In these instances the wonted consequence of Gerhardt is missed. The fact of the density of the vapour of these bodies being the same in the free as in the combined states, may have prevented him from doubling the formulæ of these anhydrous acids. The types of this theory being *essentially types of double decomposition*, this instance of simple combination diminishes somewhat the value of the otherwise great logical merit of this system.

Having taken notice of such exceptions, the empirical truth of the theory may be otherwise admitted.

[It remains to examine whether it fulfils the no less important condition that it is not found to be in disagreement with philosophical principles.]

The philosophical test demands that a theory be competent to explain the greatest number of facts in the simplest possible manner.

In applying this test, three aspects of it require to be taken into consideration :—

1. As to the extension of the theory.
2. The explanation it affords of the facts.
3. The manner of this explanation.

As to the first: this theory indeed brings every chemical combinate under a certain comparative point of view with every other. Herein apparently is its merit. Nevertheless, should our test be applied to its full extent, it will be found that it is fatal to this system, in other respects so imposing. The comparative point of view which it adopts is fundamentally false.

As to the second: it does not explain the facts at all; consequently the most essential point of the test is unfulfilled.

3. This condition of the test is in like manner unfulfilled, from the fact of the second not being complied with.

Why is it that Gerhardt's theory so signally fails in these two essential requisites? Because it is based upon an old but vicious principle, which has already retarded science for centuries. It begins with a generalization, and from this generalization deduces all the particular instances. But it does not come within the limits of a chemical paper to enter upon a discussion which is purely metaphysical. Nevertheless the theory of Gerhardt can only be combated upon metaphysical grounds, because it is only in overturning a general principle of research that the theory can be proposed.

Gerhardt's generalization lacks, moreover, the merit of being represented by a type having a known existence. $n\mathrm{O}^{\mathrm{H}}_{\mathrm{H}}$, from which he derives every chemical combinate, being in itself indefinite, cannot of course be contained or be produced in any definite body. That, however, which may be demanded of the type is, that in itself it should afford at least an instance of that which it is meant to represent. Now the part "n" of the type represents the notion of indefinite multiples of $\mathrm{O}^{\mathrm{H}}_{\mathrm{H}}$. But not a single instance of a multiple of $\mathrm{O}^{\mathrm{H}}_{\mathrm{H}}$ has been proved to exist; much less has it been proved that there exists, or can exist, multiples of this body in an indefinite series. The perfection or imperfection of the type meant to represent the generalized notion, is, however, a matter of comparatively inferior moment. It is the principle involved in this generalization which is essentially pernicious.

Should the principle which is therein adopted be applied to the common events of life, it will be found that it is simply absurd. Suppose that some one were to systematize the formation of letters into words that formed the contents of a book. Were he to begin by saying that he had discovered a *certain word which would serve as a type, and from which by substitution and double decomposition all the others are to be derived*,—that he by this means not only could form new words, but new books, and books almost *ad infinitum*,—that this word also formed an admirable point of comparison with all the others,—that in all this there were only a few difficulties, but that these might be ingeniously overcome,—he would state certainly an empirical truth. At the same time, however, his method would, judged by the light of common sense, be an absurdity. But a principle which common sense brands with absurdity, is philosophically false and a scientific blunder.

Suppose the book that had formed the basis of this system were a German one, where all the words were found to be composed at least of two letters, still even in this language the viewing and systematizing of words as a series of double decompositions would be no less ridiculous.

The sure and invincible method of arriving at every truth which the mind is capable of discovering is always one and the same. It is that, namely, of throwing away all generalization, of going back to first principles, and of letting the mind be guided by these alone. It is the same in common matters. It is the same in science. To reach the structure of words we must go back, seek out the undecomposable elements, viz. the letters, and study carefully their powers and bearing. Having ascertained these, the composition and structure of every possible word is revealed. It would be well to call to recollection the parallelism of chemical research with that of every other search after truth; for it has been in overlooking this that in chemistry false and vacillating theories have been advocated and a wrong route so often pursued. In mathematics the starting-point is not generalizations, but axioms, ultimate principles. In metaphysics, Descartes led the way of progress by analysing till he thought he could reach some ultimate elements beyond which it was impossible for him to go, then studying their force and power, and proceeding synthetically. The recognition of this method wrought the regeneration of science and philosophy.

On the other hand, look where Gerhardt's generalization of Williamson's generalization leads him, and legitimately too,—a fact which his logical spirit clearly discerned. He is led not to explain bodies according to their composition and inherent properties, but to think it necessary to restrict chemical science to the arrangement of bodies according to their decomposition, and to deny the possibility of our comprehending their molecular constitution. Can such a view tend to the advancement of science? Would it not be only rational, in accepting this veto, to renounce chemical research altogether?

These reflections naturally lead to the inquiry after another theory more adequate to satisfy the just demands which can be made upon it. There is one which, as it is still supported by many distinguished chemists, cannot be passed over altogether unnoticed. It is that of the theory of certain combinates in organic chemistry which are to be viewed as analogous to, "playing the part of," inorganic elements. These are denominated radicals, and are supposed to be contained in all organic chemical products.

In addition to this, and also in connection with it, there is a doctrine describing many combinates to be copulated, conjugated, by addition.

It is impossible here to enter upon any extensive criticism of this theory. I can only remark that it is not merely an unprofitable figure of language, but is injurious to science, inasmuch as it tends to arrest scientific inquiry by adopting the notion that these quasi elements contain some unknown and ultimate power which it is impossible to explain. It stifles inquiry at the very point where an explanation is demanded, by putting the seal of elements, of ultimate powers, on bodies which are known to be anything but this.

Science demands the strict adherence to a principle in direct contradiction to this view. That first principle, without which research cannot advance a step, dare not be ignored; namely, that a whole is simply a derivative of its parts. As a consequence of this, it follows that it is absolutely necessary to scientific unity and research to consider these bodies as entirely derivative, and as containing no secret ultimate power whatever, and that the properties which these so-called quasi elements possess are a direct consequence of the properties of the individual elements of which they are made up.

Nor is the doctrine of bodies being "conjugated by addition" a whit in advance of that which I have just been considering. This doctrine adopts the simple expedient of dividing certain combinates, if possible, into two imaginary parts, of which one or both are bodies already known. Then it tells us that these two parts are found united in this body. But how they are united, or what force binds them together, it does not inquire. Is this explication arbitrary? Is it instructive? Is it science?

I may now be permitted to submit a few considerations relative to a more rational theory of chemical combination.

As everything depends upon the method of research employed, it will in the first place be necessary to find one that may be relied upon. If the method is good and conscientiously carried out, stable and satisfactory results may be expected. If, on the contrary, it is vicious, we can only expect a corresponding issue. A satisfactory method is, however, not difficult to find, nor is it difficult in its application.

The principle which ought to guide all research is in every case the same. It is that of analysing till it is impossible to reach more simple elements, and of studying these elements in all their properties and powers. When all the properties and powers of the individual elements are known, then it will be possible to know the constitution of the combinates which their synthesis produces. It is necessary therefore in chemical research, in order to ascertain the various qualities and functions of the different elements,—

1. To consider the whole of chemistry as one.

2. To take into consideration every known combinate, and to study the character, functions, and properties displayed by each element for itself, in each of these combinates in all their different conditions and aspects. It is by a comparison of the different bodies among themselves that we are able to trace the part that is performed by each element separately.

3. To trace the general principles common to all the elements, noting the special properties of each.

This method is essentially different from that where one class of bodies is chosen as a point for the restriction of our views of the properties of the others—where only the qualities found in the first are to be measured out to the rest.

I shall now proceed to inquire how its more thorough application tends to the development of a rational chemical theory.

It has been found that there is one leading feature, one inherent property, common to all the elements. It has been denominated chemical affinity. It is discovered under two aspects:—(1) affinity of kind; (2) affinity of degree.

Affinity of kind is the special affinities manifested among the elements, the one for the other, &c., as carbon for oxygen, for chlorine, for hydrogen, &c.

Affinity of degree is the grades, or also limits of combination, which the elements display. For instance, C^2O^2 and C^2O^4 are the degrees of affinity of carbon for oxygen. C^2O^2 may be called the first degree, and C^2O^4 may be termed the second degree, and, as a higher degree than this is not known for carbon, its ultimate affinity or combining limit. Affinity of degree in an element may have only one grade. It may have, however, and generally has more than one. Here then is an inherent property common to all elements, by the removal of which the chemical character of an element will be destroyed, and by virtue of which an element finds its place marked out in a complex body.

It is such a property that is required to form the base of a system. Nor would its suitableness for this purpose be affected by the discovery that the elements are themselves composite bodies, which view the chemist is perhaps not unwarranted to adopt. For in such a case the necessity would doubtless still be found to exist of adopting the principle of affinity, or something at least equivalent to it, as the basis of the explanation of chemical combinates.

[At the moment, however, it is impossible to go back to the simpler elements. It is necessary therefore in the meantime to start from the ascertained affinities and properties amongst the elements in order to arrive at the theory of their combinates.]

In applying this method, I propose at present to consider the single element carbon. This body is found to have two highly distinguishing characteristics :—

1. It combines with equal numbers of hydrogen, chlorine, oxygen, sulphur, &c.

2. It enters into chemical union with itself.

These two properties, in my opinion, explain all that is characteristic of organic chemistry. This will be rendered apparent as I advance.

This second property is, so far as I am aware, here signalized for the first time. Evidence as to its being a property of carbon may therefore be required.

It will be found in the following:—What is the link which binds together bodies composed of 4, 6, 8, 10, 12, &c. equivalents of carbon, and as many equivalents of hydrogen, oxygen, &c.? In these you may remove perhaps all the hydrogen or oxygen, and substitute so many equivalents of chlorine, &c. It is then the carbon that is united to carbon. Further, that it is not the hydrogen that is the binding element in these combinates is evident; thus—

$$C^2\begin{matrix}H\\H\\H\\H\end{matrix}\qquad C^2\begin{matrix}\left.\begin{matrix}O\\O\end{matrix}\right\}\\\left.\begin{matrix}O\\O\end{matrix}\right\}\end{matrix}\qquad\text{and}\qquad C^2\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}$$

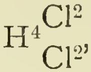
Here the whole four of hydrogen are not bound by a mutual affinity; for each element of hydrogen can be substituted for one of chlorine in regular series, beginning with the first and ending with the last. The atoms of oxygen are, on the contrary, united in pairs (which will be more fully developed hereafter), and only for two atoms of oxygen two of chlorine can be substituted; thus—

$$C^2\begin{matrix}\left.\begin{matrix}O\\O\end{matrix}\right\}\\\left.\begin{matrix}O\\O\end{matrix}\right\}\end{matrix}\qquad C^2\begin{matrix}Cl\\Cl\\\left.\begin{matrix}O\\O\end{matrix}\right\}\end{matrix}\qquad C^2\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}$$

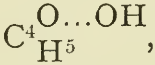
In the same manner with bodies that contain multiples of C^2 united to hydrogen, &c.

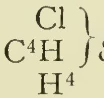
Take the inverse of this. If the four atoms of hydrogen were bound together, we could evidently expect to form such bodies as

$$H^4\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}\qquad H^4\begin{matrix}Br\\Cl\\Cl\\Cl\end{matrix}\qquad H^4\begin{matrix}Br\\Br\\Cl\\Cl\end{matrix}\qquad\text{and}\qquad H^4\begin{matrix}Br\\Br\\Br\\Cl\end{matrix}$$

or for bodies like C^4H^4, C^6H^6, C^8H^8, one would naturally expect to find the carbon substituted for chlorine, and find bodies like  $H^{4}{}^{Cl^{2}}_{Cl^{2}}$, H^6Cl^6, H^8Cl^8 &c.

These bodies are not only unknown, but the whole history of hydrogen might be investigated and not a single instance be found to favour the opinion that it has any affinity for itself when in union with another element.

Now, on the other hand, carbon remains chemically united to carbon, while perhaps 8 equivalents of hydrogen are exchanged for 8 equivalents of chlorine, as in naphthaline. Analogous to this is the conversion of alcohol,  $C^{4}{}^{O\ldots OH}_{H^{5}}$, and the hydrocarbide C^4H^6 into C^4Cl^6. All the countless instances of substitution of chlorine, &c. tend in the same direction. They prove beyond doubt that carbon enters into chemical union with carbon, and that in the most stable manner. This affinity, one of the strongest that carbon displays, is perhaps only inferior to that which it possesses for oxygen.

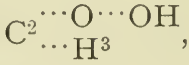
Another feature in the affinity of carbon is, that it combines by degrees of two; thus, C^2O^2 and C^2O^4, C^4H^4 and C^4H^6, C^6H^6 and C^6H^8, C^8H^8 and C^8H^{10}, &c.: from these last it is especially evident that two is the combining grade of carbon. It becomes still more apparent when we compare the bodies C^4H^4 and C^4H^5Cl, that is,  $C^{4}\begin{matrix}Cl\\H\\H^{4}\end{matrix}\Big\}$ &c. Many such proofs might be added, while on the other hand there are no instances contradictory of this point. Hence the circumstance that it must ever remain impossible to isolate a combinate of the form C^2H^3 or C^4H^5, &c.

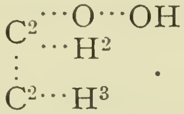
Carbon having only two grades of combination of two atoms each, a fact which is easily traced throughout all organic chemistry, this inherent property of the element may legitimately furnish two grand types for all its combinates.

The first type will be $nC^{2}M^{4}$.

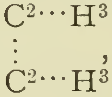
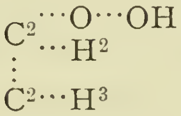
The second type will be $nC^{2}M^{4}—mM^{2}$.

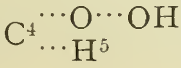
As examples belonging to the first type, may be mentioned the alcohols of the æthylic form, their æthers, the fatty acids, &c.

Thus methylic alcohol has the formula  $C^{2}\begin{array}{l}\cdots O\cdots OH\\ \cdots H^{3}\end{array}$,

and æthylic alcohol,  $\begin{array}{l}C^{2}\begin{array}{l}\cdots O\cdots OH\\ \cdots H^{2}\end{array}\\ \vdots\\ C^{2}\cdots H^{3}\end{array}$.

In these instances it will be observed that for each double atom of carbon the combining power is (4) four, which is the ultimate limit of combination for carbon in all bodies yet produced.

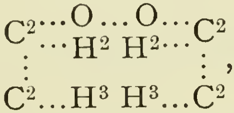
In the latter instance it is apparent, inasmuch as if the combining limit of two C^{2}s be each reduced by 3 in hydrogen or oxygen, there still remains a combining power of *one* to each of the two C^{2}s which each expends in uniting with the other; therefore  $\begin{array}{l}C^{2}\cdots H^{3}\\ \vdots\\ C^{2}\cdots H^{3}\end{array}$, or what is the same thing,  $\begin{array}{l}C^{2}\begin{array}{l}\cdots O\cdots OH\\ \cdots H^{2}\end{array}\\ \vdots\\ C^{2}\cdots H^{3}\end{array}$ belongs to the type $nC^{2}M^{4}$.

Again, the inherent properties of the elements may be viewed as dividing bodies into primary, secondary, tertiary, and so on combinates. These may be termed so many orders of complicity. Thus $C^{4}H^{6}$ is a primary combinate, or it belongs to the first order of complicity; but  $C^{4}\begin{array}{l}\cdots O\cdots OH\\ \cdots H^{5}\end{array}$ is a secondary combinate, or belongs to the second order of complicity. C^2O^2 and C^2O^4 are primary, while $C^2O^4, 2OH$ and $C^2O^4, 2OKa$ are secondary.

A primary combinate is then nC^2 united to nM^4 or to $nM^4—mM^2$ in such a manner that the combining energy of the complement (nM^4, &c.) either *potentially or actually* does not extend beyond nC^2.

A secondary combinate is one in which the combining energy of the complement is not all expended upon nC^2, but is extended further to one or more elements.

On the same principle there are tertiary combinates, &c.

These orders of complicity ought in reality to be subdivided. This, however, I do not think it necessary for the present to enter upon. It will now be understood why an alcohol belongs to the type nC^2M^4, and on the same principle why a free æther belongs to the same type, thus 

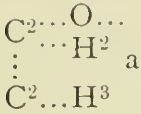
$$\begin{array}{lcr} C^2\cdots O\ldots & & O\cdots C^2 \\ \vdots\quad\cdots H^2 & & H^2\cdots\quad\vdots \\ C^2\ldots H^3 & & H^3\ldots C^2 \end{array}$$

, while they are at the same time secondary combinates.

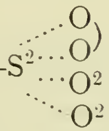
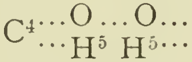
A secondary combinate, that is to say, a body belonging to the second order of complicity, is, as will be understood from the principle which forms the ground of the rational theory, a direct consequence of an inherent property of one or more of the elements which form the complement to the carbon.

In the instance before us, it is a certain property of the oxygen which is the cause of the secondary combinate. This property is the affinity which one atom of oxygen in combination always exerts towards another atom of oxygen likewise in combination.

This affinity is modified by the electric position of the element to which the respective atoms of oxygen are bound. From this property results the fact, that in organic combinates the atoms of oxygen are always found double.

For instance, the combining limit of oxygen being two, when two molecules of  $\begin{array}{l} C^2\cdots O\cdots \\ \vdots \quad \cdots H^2 \\ C^2\ldots H^3 \end{array}$ are set at liberty, the free affinities of the oxygen instantly produce the union of these molecules. The cause of the union of two molecules of C^2H^3 has been already remarked. In the two cases, the causes of the union of the respective molecules are in so far different, that the one is the result of a property of the carbon, while the other is the result of a property of the oxygen.

The view here adopted of the nature of oxygen is, I am convinced, alone in conformity with the reactions where the properties of this body develope themselves.

The vapour of anhydrous sulphuric acid, for instance, is conducted into anhydrous æther. The following will then be the reaction :— $S^2 \begin{array}{l} \cdots O \\ \cdots O \\ \cdots O^2 \\ \cdots O^2 \end{array}$ entering into communication with  $C^4 \begin{array}{l} \cdots O\ldots O\cdots \\ \cdots H^5 \; H^5\cdots \end{array} C^4$, the two atoms of the oxygen of the sulphuric acid and the two atoms of the oxygen of the æther (now in presence of each other) being in different (perhaps different electric) conditions, mutually loosen their former affinities and reunite themselves to the (electrically?) different atoms of oxygen of these respective combinates.

The same principle may naturally be expected to display itself with regard to acids and bases. The oxygen of an acid unites itself to the (electrically?)

different oxygen of water. The oxygen of a base on the same principle has an affinity for the electrically different oxygen of water.

It will be observed—

1. That the oxygen of the water of an acid can only be expelled by that of a base, and *vice versâ*.

2. It is to be remarked that *it is not* the metal of a base which exchanges places with the hydrogen of the hydrate of an acid; for if that were the case, the affinity of the oxygen of the metal, and also of the acid, *would be greater for the oxygen of the water* than the affinity of the hydrogen for that same oxygen. But this is not so. The very opposite is the truth. If one atom of hydrogen be withdrawn from the hydrate of an acid or from *the hydrate of an oxide, it is universally accompanied by an atom of oxygen.* It is evident, then, that the affinity between *the positive and negative atoms of oxygen is less than that which attaches these atoms to the element with which they form a primary combinate.*

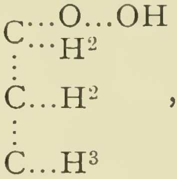
A consequence of this truth is, that it is impossible to double the equivalent of oxygen, if the chemical equivalents are to be understood as not being in direct contradiction to any chemical truth or essential feature in the properties of an element. Carbon differs entirely in this respect from oxygen.

There is no reaction found where it is known that C^2 is divided into two parts. It is only consequent therefore to write, with Gerhardt, C^2 simply as C, it being then understood that the equivalent of carbon is (12) twelve.

This value of the atom will be adopted in the following part of this paper.

Sulphur, selenium, &c. being bodies displaying properties similar, not to carbon, but to oxygen, it will be necessary to retain the equivalent value that has generally been assigned to them.

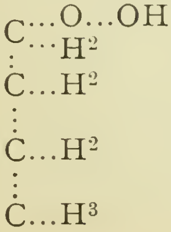
I have now shown how ordinary alcohol, $C^2H^6O^2$, common æther, and the hydrocarbide, C^2H^6, belong to the type nCM^4. The phænomena which necessitate this view of the constitution of these bodies have a like consequence in regard to the other alcohols, glycols, acids, and æthers of this series.

Propyle alcohol is 

$$\begin{array}{l} C\ldots O\ldots OH \\ \vdots\ \cdots H^2 \\ C\ldots H^2 \\ \vdots \\ C\ldots H^3 \end{array}$$

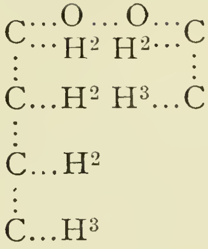
, where it will be seen that the atom of carbon situated between the two others, on account of being chemically united to these, is reduced to the combining power of two for hydrogen, oxygen, &c. One combining power is given up to the carbon upon the one side, and a second to the carbon upon the other.

It will be observed also, that the primary combinates ought in rigour to be themselves enumerated in an inverse order. The type nCM^4 becomes then in reality the type CM^4. This enumeration, however, does not appear to possess any great practical utility, and it is perhaps preferable simply to denote it in an indefinite manner by adding "n" to the true type CM^4.

In like manner the butyle alcohol is to be viewed as 

$$\begin{array}{l} C\ldots O\ldots OH \\ \vdots\ \cdots H^2 \\ C\ldots H^2 \\ \vdots \\ C\ldots H^2 \\ \vdots \\ C\ldots H^3 \end{array}$$

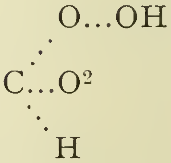
, and so on throughout all the series of these alcohols. The constitution of the æthers will be evident:



$$\begin{array}{l}\mathrm{C}\begin{array}{l}\cdots\mathrm{O}\cdots\mathrm{O}\cdots\\ \cdots\mathrm{H}^2\ \mathrm{H}^2\cdots\end{array}\mathrm{C}\\ \vdots\qquad\qquad\qquad\ \vdots\\ \mathrm{C}\cdots\mathrm{H}^2\ \mathrm{H}^3\cdots\mathrm{C}\\ \vdots\\ \mathrm{C}\cdots\mathrm{H}^2\\ \vdots\\ \mathrm{C}\cdots\mathrm{H}^3\end{array}$$

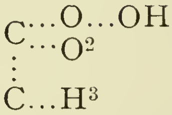
represents the mixed butylic-ethylic æther.

Formic acid is represented by the form



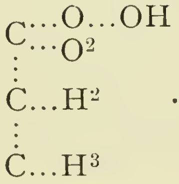
$$\mathrm{C}\begin{array}{l}\cdots\mathrm{O}\cdots\mathrm{OH}\\ \cdots\mathrm{O}^2\\ \cdots\mathrm{H}\end{array}$$

; acetic acid in like manner,



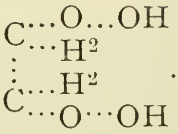
$$\begin{array}{l}\mathrm{C}\begin{array}{l}\cdots\mathrm{O}\cdots\mathrm{OH}\\ \cdots\mathrm{O}^2\end{array}\\ \vdots\\ \mathrm{C}\cdots\mathrm{H}^3\end{array}$$

. Propionic acid is



$$\begin{array}{l}\mathrm{C}\begin{array}{l}\cdots\mathrm{O}\cdots\mathrm{OH}\\ \cdots\mathrm{O}^2\end{array}\\ \vdots\\ \mathrm{C}\cdots\mathrm{H}^2\\ \vdots\\ \mathrm{C}\cdots\mathrm{H}^3\end{array}$$

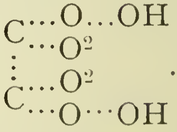
. The constitution of glycol may be represented as follows:—



$$\begin{array}{l}\mathrm{C}\begin{array}{l}\cdots\mathrm{O}\cdots\mathrm{OH}\\ \cdots\mathrm{H}^2\end{array}\\ \vdots\\ \mathrm{C}\begin{array}{l}\cdots\mathrm{H}^2\\ \cdots\mathrm{O}\cdots\mathrm{OH}\end{array}\end{array}$$

.

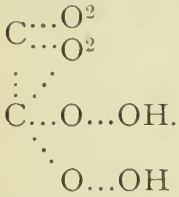
In like manner as to the acids of these glycols; oxalic acid, for instance, may be represented as



$$\begin{array}{l}\mathrm{C}\begin{array}{l}\cdots\mathrm{O}\cdots\mathrm{OH}\\ \cdots\mathrm{O}^2\end{array}\\ \vdots\\ \mathrm{C}\begin{array}{l}\cdots\mathrm{O}^2\\ \cdots\mathrm{O}\cdots\mathrm{OH}\end{array}\end{array}$$

.

Respecting these acids, it may perhaps be allowable to suggest the possibility of the molecule having two poles, and that especially the atom of oxygen situated at one or perhaps both, and near to two atoms of oxygen bound together, and forming no secondary combinate, may be in a state presenting great affinity for basic oxygen. Analogy with the electric poles may perhaps demand the opinion that all the negative oxygen be situated upon one side of the molecule. It will in that case be preferable to represent the oxalic acid as



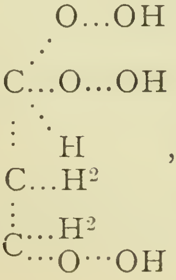
Be that as it may, however, the rational method of investigation proves it to be a law, that in acids of the type nCM^4 the presence of two atoms of oxygen bound together so as to form only a primary part of the same molecule, and situated close to the negative oxygen, is necessary to the calling forth or production of this negative state.

This is a particular instance, but it moreover *shows generally how the electro-positive or the electro-negative value of the elements mutually modify and condition the electro-positive or electro-negative value* of each other when in combination.

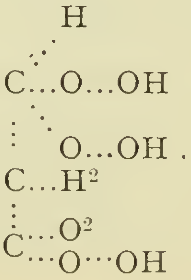
This law is different from the electric hypothesis which chemists have formerly defended, but which never could be traced throughout a thoroughgoing application of their views to organic chemistry.

The law here distinctly enounced coincides exactly with, and is rendered apparent by the application of the theory of chemical combination which I support.

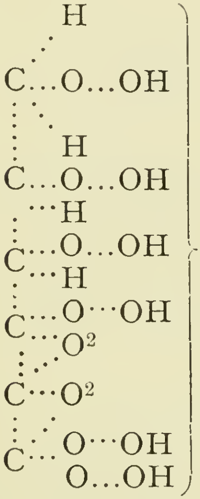
But to return. Glycerine is



, and glyceric acid

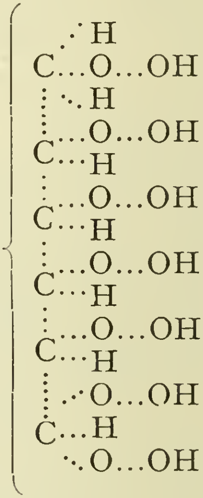


Glucose has been perhaps too little investigated to afford data sufficient to determine definitely its formula. Taking, however, mucic and saccharic acids as starting-points, these bodies may be meanwhile represented as—



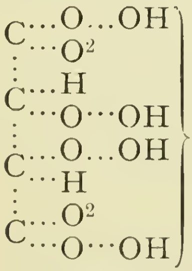
the acids.

Glucose.

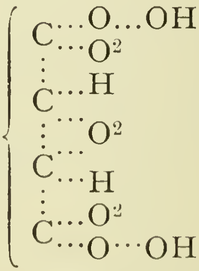


It will thus be seen that these combinates all belong to the type nCM^4.

Many others might be added. For instance, tartaric acid :—



And the bibasic acid produced from it by the action of heat will be perhaps



tartrelic acid.

It is my intention to consider, in a future communication, the second type, and to apply my views to the cyanogen combinates, &c.

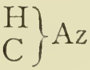
[*The following paragraphs, forming the conclusion to the French version of this paper, are not included in the English version.*]

[In the meantime I shall only add the way in which I regard the constitution of the principal cyanogen compounds.

Reasons altogether similar to those that make me regard 4 as the limit of the combining power of carbon, lead me to assign 5 as the limit of combination of nitrogen. The first degree of combination of this element is met with in ammonia and equals 3. The second, which is equal to 5, is found, amongst other chemical compounds, in the chloride and in the oxide of ammonium, as well as in nitric acid.

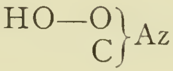
From this it follows that carbon and nitrogen combined in such manner that both attain the limits of their combining power, will form a body, the free affinity of which will be exerted in fixing one equivalent of hydrogen or of another element.

Thus the formula of hydrocyanic acid will be



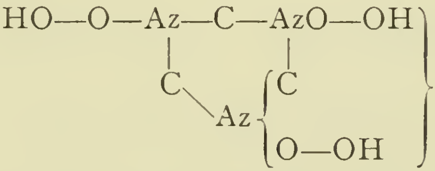
$$\left.\begin{matrix}\mathrm{H}\\\mathrm{C}\end{matrix}\right\}\mathrm{Az}$$

Cyanic acid will be



$$\left.\begin{matrix}\mathrm{HO{-}O}\\\mathrm{C}\end{matrix}\right\}\mathrm{Az}$$

cyanuric acid



In this last formula the atoms of carbon and of nitrogen are linked by 2 units of affinity and not by 4 as in the first two examples.]

RESEARCHES ON SALICYLIC ACID.*

THE researches which I have the honour to submit to the Academy have for their subject the action of perchloride of phosphorus on salicylate of methyl. I have undertaken them with the object of throwing some light upon a disputed question: the constitution and the basicity of salicylic acid.

A violent action occurs on the contact of oil of gaultheria with perchloride of phosphorus. In order to control this, it is necessary to add the essential oil in small portions to the perchloride in the proportion of 1 equivalent of the former body to 2 equivalents of the latter. Hydrochloric acid and chloride of methyl are disengaged during the whole course of the operation.

The product obtained is submitted to fractional distillation. Only a trace of oxychloride passes over: a considerable excess of perchloride of phosphorus afterwards distils, and when the temperature has reached 160 degrees the residue forms a black liquid. If the distillation be continued, the temperature rises rapidly to 285 degrees. The larger portion of the product passes between 285 and 295 degrees, in the form of a colourless or slightly yellow-coloured liquid. It is collected separately. A black mass remains which solidifies on cooling.

---

* [From Comptes rendus, **46** (1858), 1107-1110.]

The liquid collected about 290 degrees gave on analysis the following results :

	Experiments.			Theory.
Carbon,	30·86	29·4	29·9	30·65
Hydrogen,	1·58	1·59	1·51	1·46
Chlorine,	41·01	41·05	...	38·86
Phosphorus,	12·2	...	...	11·5

The composition of the body is represented by the formula

$$C^{14}H^{4}Cl^{3}PhO^{6}.$$

It is formed by the following reaction :

$$\underbrace{C^{16}H^{8}O^{6}}_{\text{Essence of gaultheria.}} + PhCl^{5} = HCl + \underbrace{C^{2}H^{3}Cl}_{\text{Chloride of methyl.}} + \underbrace{C^{14}H^{4}Cl^{3}PhO^{6}}_{\text{Terchlorophosphate of salicyl.}}$$

I have satisfied myself that terchlorophosphate of salicyl is also generated by the action of perchloride of phosphorus on salicylic acid

$$\underbrace{C^{14}H^{6}O^{6}}_{\text{Salicylic acid.}} + PhCl^{5} = 2HCl + \underbrace{C^{14}H^{4}Cl^{3}PhO^{6}}_{\text{Terchlorophosphate of salicyl.}}$$

The reaction is less violent between the two solid bodies than with the essence. Hydrochloric acid is disengaged and when the action is ended the residue is the same as that obtained with oil of gaultheria. The two products distil in exactly the same manner and at the same temperature, and the liquids obtained possess the same composition and the same properties.

The terchlorophosphate of salicyl obtained by one or other of these processes soon decomposes in contact with cold water, and immediately when it is boiled with this liquid. The products of this reaction are hydrochloric acid, phosphoric acid, and salicylic acid.

$$\underbrace{C^{14}H^{4}Cl^{3}PhO^{6}}_{\substack{\text{Terchlorophos-}\\ \text{phate of salicyl.}}} + 8HO = \underbrace{PhH^{3}O^{8}}_{\substack{\text{Phosphoric}\\ \text{acid.}}} + 3HCl + \underbrace{C^{14}H^{6}O^{6}}_{\substack{\text{Salicylic}\\ \text{acid.}}}$$

I have satisfied myself by an analysis that salicylic acid is really formed in this reaction and not monochlorobenzoic acid. When terchlorophosphate of salicyl is rapidly distilled it partly decomposes, emitting abundant vapours of hydrochloric acid. Above 300 degrees, a liquid body passes which, when it is preserved for some days in a closed tube, deposits large crystals which contain :

	Experiments.		Theory.
Carbon,	40·2	39·16	38·44
Hydrogen,	2·3	1·96	1·83
Chlorine,	17·07	...	16·25

This analysis, the mode of formation of the crystals and especially their breaking up into two parts by water, as I am about to point out further on, lead me to assign to them the composition represented by the following formula :

$$C^{14}H^{4}O^{8}ClPh.$$

As this substance, which I call monochlorophosphate of salicyl, decomposes in the air, from which it attracts moisture, and as it is formed besides from a liquid boiling at a very high temperature, I have not entertained the idea of obtaining it in a purer condition and have been obliged to content myself with the foregoing analysis.

The slow action that I have just described which moisture exerts upon the products, at once chlorinated and phosphorated, confirms the composition that I ascribe to them. When exposed to the air they attract water vapour from it by degrees; the chlorine that they contain combines with the hydrogen and is replaced by the oxygen. A new acid is thus formed which I call phosphosalicylic acid, and of which the composition is expressed by the formula

$$C^{14}H^{7}PhO^{12}.$$

This product, which is solid, gave on analysis the following results:

	Experiments.	Theory.
Carbon,	38·05	38·53
Hydrogen,	3·39	3·21
Phosphorus,	14.48	14·22

It is formed by the following reactions:

$$\underbrace{C^{14}H^{4}Cl^{3}PhO^{6}}_{\text{Terchlorophosphate of salicyl.}} + 6HO = 3HCl + \underbrace{C^{14}H^{7}PhO^{12}}_{\text{Phosphosalicylic acid.}}$$

$$\underbrace{C^{14}H^{4}ClPhO^{8}}_{\text{Monochlorophosphate of salicyl.}} + 4HO = ClH + C^{14}H^{7}PhO^{12}$$

Phosphosalicylic acid is a tribasic acid. It may be looked upon as a conjugated combinate of phosphoric acid and salicylic acid

$$PhH^{3}O^{8} + C^{14}H^{6}O^{6} = C^{14}H^{7}PhO^{12} + 2HO.$$

The experiments which I have just briefly described do not agree in all points with the observations that have been published on the same subject by Gerhardt,[*] Chiozza,[†] and Drion.[‡] In particular, they appear to cast some doubts upon the existence of Gerhardt's chloride of salicyl, a product that has never been analysed. We shall direct attention to the fact moreover that the formation of this product by the action of perchloride of phosphorus on salicylic acid or on oil of gaultheria, should be accompanied by that of oxychloride of phosphorus. Now, in the reactions in question there is formed no more than traces of this substance, as indeed the authors whom we quote indicate elsewhere. Whether the divergences that we point out depend upon some chance circumstance or upon the special conditions in which the observers are placed, this is what new experiments will require to decide.

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[*] *Comptes rendus*, t. xxxviii., p. 34.

[†] *Annales de Chimie et de Physique* (3e série), t. xxxvi., p. 102.

[‡] *Comptes rendus*, t. xxxix. [(1854), p. 122.]

RESEARCHES ON SALICYLIC ACID.*

CONFLICTING opinions being entertained among chemists respecting the constitution and basicity of salicylic acid, in order, if possible, to throw some additional light upon this question, I have been induced to undertake the investigation of the action of two equivalents of pentachloride of phosphorus upon the salicylate of methyl.

When these two bodies are brought into contact, the reaction which ensues is exceedingly violent, and it is necessary to add very gradually the one equivalent of oil of gaultheria to the two equivalents of perchloride of phosphorus. Vapour of hydrochloric acid, mingled with that of the chloride of methyl, is disengaged during the whole course of the operation.

The residue of this reaction is submitted to distillation. A trace of oxychloride passes over, and is followed by something approaching to an equivalent of the perchloride of phosphorus.

The temperature having now risen to about 160°, the residue has darkened in colour. Submitted to a further distillation, a colourless or slightly yellow liquid passes over, while the temperature rises rapidly to about 285° and 295° Cent. The portion passing between these temperatures is collected apart. It constitutes the larger part of the product of distillation. There remains a pitchy residue, which solidifies on cooling. The liquid collected,

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[* From The Edinburgh New Philosophical Journal, New Series, 8, (1858), 213-217.]

as described, on being submitted to analysis, furnished the following results :—

1. 0·41 grms. of substance gave 0·464 grms. of carbonic acid, and 0·0585 grms. of water.

2. 0·49 grms. of substance gave 0·528 grms. of carbonic acid, and 0·0705 grms. of water.

3. 0·515 grms. of substance gave 0·565 grms. carbonic acid, and 0.071 grms. of water.

1. 0·0438 grms. of substance gave 0·7595 grms. of chloride of silver.

2. 0·34 grms. of substance gave 0·563 grms. of chloride of silver.

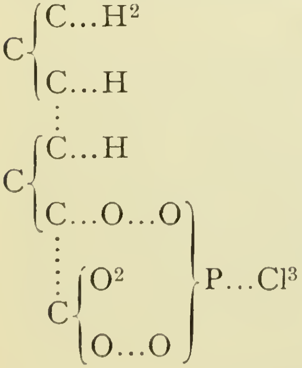
1. 0·651 grms. of substance gave 0·283 grms. of the pyrophosphate of magnesia.

These analyses lead to the crude formula,—

$$C^7H^4Cl^3PO^6.$$

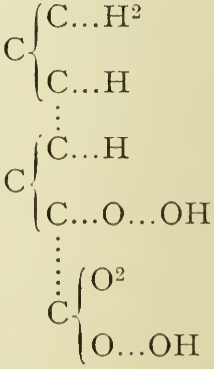
	Found.			Calculated.
	I.	II.	III.	
Carbon,	30·86	29·4	29.9	30·65
Hydrogen,	1·58	1·59	1·51	1·46
Chlorine,	41·01	41·05	...	38·86
Phosphorus,	12·2	...	...	11·5

According to the rational theory which I seek to develop in another paper,* the constitution of this body may be represented as :—



$$\begin{array}{l} C\left\{\begin{array}{l} C\ldots H^2 \\ C\ldots H \end{array}\right. \\ \vdots \\ \left.\begin{array}{l} C\left\{\begin{array}{l} C\ldots H \\ C\ldots O\ldots O \end{array}\right. \\ \vdots \\ C\left\{\begin{array}{l} O^2 \\ O\ldots O \end{array}\right. \end{array}\right\} P\ldots Cl^3 \end{array}$$

It is a tertiary derivative; the secondary derivative, salicylic acid, being,



$$\begin{array}{l} C\left\{\begin{array}{l} C\ldots H^2 \\ C\ldots H \end{array}\right. \\ \vdots \\ C\left\{\begin{array}{l} C\ldots H \\ C\ldots O\ldots OH \end{array}\right. \\ \vdots \\ C\left\{\begin{array}{l} O^2 \\ O\ldots OH \end{array}\right. \end{array}$$

---

* Lond. Phil. Mag., August 1858.

The reaction of which this body is the result is represented by the following equation [*]:—

$$C^7H^6O^6 + PCl^5 - 2HCl = C^7H^4Cl^3PO^6.$$

This is the same body which, unpurified, Gerhardt calls the chloride of salicyl,[†] and Chiozza the chloride of chlorobenzoïl,[‡] or the hydrochlorate of monochlorobenzoic acid. In order to determine rigorously whether the body produced by Chiozza from salicylic acid was really the same as that which Gerhardt and I have obtained from the oil of gaultheria, I investigated the action of the perchloride of phosphorus upon the pure acid. The reaction which takes place between the two solid bodies is less violent than when the oil was employed. Nevertheless, in this instance also the action is prompt. After the vapour of hydrochloric acid has passed off, the residue in the flask is identical with that which remains when the oil of gaultheria is employed. These two products distil in identically the same manner, with the same physical appearances, while the products of distillation produce exactly the same results upon analysis.

These products display also entirely the same results in all their reactions.

The terchlorophosphate of salicyl obtained by either process is very soon decomposed by water in the cold, and immediately, upon the application of heat, the products being hydrochloric, phosphoric, and salicylic acids.

Chiozza's monochlorobenzoic acid, which he believes to be produced along with hydrochloric acid in the decomposition of this body, is only salicylic acid* rendered impure by hydrochloric and phosphoric acids.

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[*] [Couper gives here the equation representing the action of PCl_5 on salicylic acid (of which he speaks a few lines further on) instead of that for the action on gaultheria oil.]

[†] Compt. Rend. de l'Acad. xxxviii. 34.

[‡] Ann. de Chim. et de Phys. [3] xxxvi. 102.

Chiozza did not succeed in producing the reaction for salicylic acid by the perchloride of iron. Nor is it to be observed till the liquid containing the phosphoric acid is separated from the crystals of salicylic acid, but as soon as this is done, the application of the test gives the intense and characteristic colour produced by the acid in question. An analysis which I have made confirms this result.

0·301 grms. of these crystals, expressed between folds of bibulous paper, re-crystallised from water, and dried, upon combustion, gave 0·668 grms. of carbonic acid, and 0·116 grms. of water.

	Found.	Calculated.
Carbon,	60·52	60·86
Hydrogen,	4·27	4·34

In another analysis 0·2205 grms. of substance gave 0·4885 grms. of carbonic acid, and 0·0875 grms. of water, which, calculated, gives—

60·42 % for carbon, and 4·4 % for hydrogen.

This acid agrees also in all its physical aspects with the salicylic acid.

It is evident, then, that those three bodies,—namely, the chloride of salicyl of Gerhardt, the chloride of chlorobenzoil, and the chlorobenzoilic acid of Chiozza, are not yet known.

When the terchlorophosphate of salicyl is quickly distilled, hydrochloric acid is given off in considerable quantity, while the body, at the same time, acquires a dark colour. The last portion of the product of this distillation, which passes at a temperature above 300° Cent., being allowed to stand for a day or two in a closed tube, deposits large crystals, which having been pressed between folds of bibulous paper, and submitted to analysis, gave the following results:—

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* [Couper is mistaken in this. Chiozza certainly had in his hands chlorobenzoyl chloride and chlorobenzoic acid.]

1°. 0·3565 grms. of substance gave 0·5255 carbonic acid, and 0·074 grms. water.

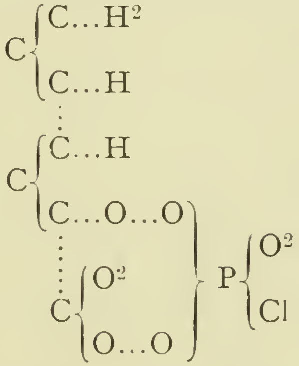
2°. 0·57 grms. of substance gave 0·826 grms. carbonic acid, and 0·101 grms. of water.

1°. 0·255 grms. of substance gave 0·176 grms. of chloride of silver.

Compared with the crude formula $C^7H^4O^8ClP$, these results will be:—

	Found.		Calculated.
	I.	II.	
Carbon,	40·2	39·16	38·44
Hydrogen,	2·3	1·96	1·83
Chlorine,	17·07	...	16·25

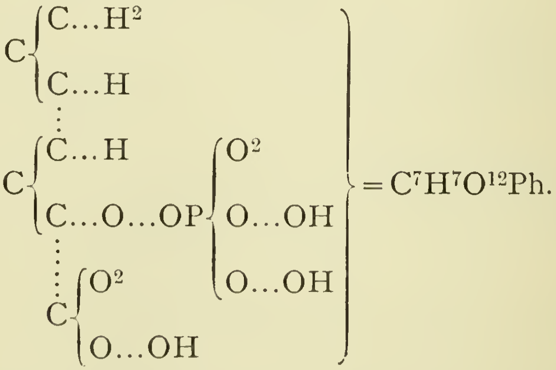
The rational formula is,—



The monochlorophosphate of salicyl being a body which is quickly decomposed by exposure to the air, and only to be obtained from a liquid passing at an exceedingly high temperature, I did not think it easily possible to obtain a purer body, and have contented myself with the above analysis. Although these analyses might in themselves leave some doubt as to the composition of the body, still, when taken in connection with a combinate which I am about to describe, and which is produced from the monochlorophosphate of salicyl, as well as from the terchlorophosphate, I think I may be warranted in ascribing definitely to it the above formula.

This compound is produced by the exposure to the atmosphere of the bodies just mentioned. The chlorine contained in them decomposes the water of the atmosphere combining with an equivalent of hydrogen, while the oxygen is taken up by the bodies in question in replacement of the chlorine. This new oxygen, however, enters into the state in which it is found in acids, and has a great affinity for the oxygen of water and bases. It therefore attracts the water of the atmosphere, and the combinate becomes an hydrated acid.

This body being submitted to analysis, gave results according with the rational formula :—*



$$\left.\begin{array}{l} C\left\{\begin{array}{l} C\ldots H^{2}\\ C\ldots H\end{array}\right.\\ \vdots\\ C\left\{\begin{array}{l} C\ldots H\\ C\ldots O\ldots OP\left\{\begin{array}{l} O^{2}\\ O\ldots OH\\ O\ldots OH\end{array}\right.\end{array}\right.\\ \vdots\\ C\left\{\begin{array}{l} O^{2}\\ O\ldots OH\end{array}\right.\end{array}\right\}=C^{7}H^{7}O^{12}Ph.$$

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* [Kekulé stated erroneously (Lehrbuch, 4, 171) that Couper did not give constitutional formulæ for the three phosphorus compounds described in this paper. Evidently he had only seen the Comptes Rendus note and was not aware of the existence of the extended formulæ that were included in the longer English paper.]

1°. 0·2845 grms. of substance gave 0·397 grms. of carbonic acid, and 0·086 grms. of water.

0·1785 grms. of substance gave 0·103 grms. of the pyrophosphate of magnesia.

	Found.	Calculated.
Carbon,	38·05	38·53
Hydrogen,	3·39	3·21
Phosphorus,	14·48	14·22

This phosphosalicylic acid is a tribasic acid, and forms insoluble salts with baryta, lead, and silver, containing three equivalents of these metals.

I propose taking into consideration more fully the constitution of salicylic acid in a subsequent communication. The formula here given of that body may be in the meanwhile suggestive.

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